An Assessment of Indoor Air Quality at Two Contrasting Location and Building Ventilation Types in London

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AN ASSESSMENT OF INDOOR AIR QUALITY AT TWO CONTRASTING LOCATION AND BUILDING VENTILATION TYPES IN LONDON

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DECLARATION

I, **MohdShukri Bin MohdAris** declare that all the work submitted in this thesis is my own word and that all references are cited accordingly.

Signed: _____ (student)

Date: _____

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LIST OF ACRONYMS

AA	ascorbic acid / ascorbate
AER	air exchange rate
AURN	Automatic Urban and Rural Network
BAL	bronchoalveolar lavage
BRE	Building Research Establishment
CI	confident interval
CO	carbon monoxide
CPC	carbon particle counter
Defra	Department for Environment, Food and Affairs
DMA	dynamic mechanical analyser
DTNB	5,5'-Dithiobis(2-nitrobenzoic acid)
EPAQS	The Expert Panel on Air Quality Standard
ET	extrathoracic
ETS	environmental tobacco smoke
EU	European Union
EXPOLIS	Air Pollution Exposure Distributions of Adult Urban Population in Europe
GSH	reduced glutathione
GSSG	glutathione disulphide
GSTP1	glutathione S-transferase P
GSx	total glutathione (GSH + GSSG)
HCl	hydrochloric acid
HPLC	high pressure liquid chromatography
HVAC	heating, ventilation and air conditioning
IAQ	indoor air quality
IL	interleukin-8 / interleukin-9
KCL	King's College London
LAQN	London Air Quality Network
LPM	litre per minute
MFG	micro fibre glass
MPA	metaphosphoric acid
NADPH	β-nicotinamide adenine di-nucleotide phosphate (reduced form)
$NADP^+$	nicotinamide adenine dinucleotide phosphate
NaOH	sodium hydroxide
NDIR	non-dispersive infrared sensor
NH_3	ammonia
NIOSH	National Institute for Occupational Safety and Health
NO	nitric oxide
NO_2	nitrogen dioxide
NO_X	nitrogen oxide ($NO + NO_2$)
NM	nucleation mass median
NPL	National Physic Laboratory
O_3	ozone
PAH	polycyclic aromatic hydrocarbon
PGE_2	prostaglandin E_2

PM	particulate matter
$PM_{0.1}$	particles with an aerodynamic diameter less than 0.1 µm or ultrafine particle
PM_1	particles with an aerodynamic diameter less than 1 µm
PM_{10}	particles with an aerodynamic diameter less than 10 µm
$PM_{2.5}$	particles with an aerodynamic diameter less than 2.5 µm
$PM_{0.1-2.5}$	particles with an aerodynamic diameter from 0.1 to 2.5 µm
$PM_{2.5-10}$	particles with an aerodynamic diameter from 2.5 to 10 µm
PMN	polymorphonuclear
PTFE	polytetrafluoroethylene
PU	pulmonary
PVC	polyvinyl chloride
RAPTES	Risks of Airborne Particles: a Toxicological and Epidemiology hybrid Study
ROS	reactive oxygen species
RTLF	respiratory tract lining fluid
SAM	surface area median
SBS	sick building syndrome
SD	standard deviation
SMPS	scanning mobility particle size
SO_2	sulphur dioxide
TB	tracheobronchial
TBC	total bacterial count
TEOM	tapered elemental oscillatory microbalance
TNB	5-thio-2-nitrobenzoic acid ion
UA	uric acid
UFP	ultrafine particle
UKAS	United Kingdom Accreditation Service
US EPA	United State Environmental Protection Agency
VOCs	volatile organic carbon species
WHO	World Health Organisation

ABSTRACT

Background: People spend most of their time indoors, in buildings such as schools and offices, as well as their homes. Recent interest in Indoor Air Quality (IAQ) suggests that the contribution of outdoor pollutants and indoor airborne particulate and gaseous pollutants may be responsible for the aggregation of a number of respiratory illnesses. Because of these possible health implications, it is important to understand the characteristics of each air pollutant inside/outside (I/O) the building and the variables affecting the degree of exposure to them. **Objectives:** This was achieved by long-term monitoring of a range of pollutants at two contrasting building types and locations within London. The transfer of pollutants(NO_X, NO_2, O_3 and PMs) and particulate toxicity (PM_{TSP}) within I/O sources over a wide range of meteorological condition, occupancy and seasonality was then characterised. **Results 1 (Case 1):** At naturally ventilated school building (urban background), paired long term monitoring revealed that the indoor gaseous pollutant concentration reacted differently according to occupancy and seasonality. Due to the fact that indoor NO concentration in the classroom was possibly dominated by indoor source, its presence was also believed to play an important role of reducing O_3 in the classroom which mainly came attributed from outdoors during summer time. The increment of indoor larger (PM_{10}) and coarse particle ($PM_{2.5-10}$) was attributed when the building was actively used and identified to be linked from the certain type of classroom activity. However, a greater proportion of indoor $PM_{2.5}$ was contributed from outdoors. **Results 2 (Case 2):** In contrast, a different pattern of diurnal variation profiles was observed in the mechanically ventilated office building (roadside site). An extreme indoor concentration of indoor NO_X and NO_2 monitored during rush hour on working-days were explained by the outdoor penetration. An extension study (building improvement) showed a clear reduction pattern in PM concentration; however it did not solve the high NO_2 problem. **Results 3:** The novel time series of oxidative potential (OP) dataset established in this study highlightedaclear difference between the two sites. Indoor OP metrics in the roadside building recorded higher depletion rates compared to the urban background site. At urban background site, when indoor OP dataset were categorised and group as building occupancy and seasonal dependent, the indoor PM OP antioxidants metrics was found to have a higher depletion rate during occupied period and was observed during winter time, which particularly in

particulate mass metric. At roadside site, interestingly, a significant decrease in PM-induced antioxidant depletion indoors, observed after the door upgrade. This study demonstrated that PM OP analysis from both internal and external sources is a useful tool for illustrating any changes in sources in the transfer of pollutants into a building.

Conclusion: These monitoring results reveal the complexity of internal-external air quality relationship within building envelopes referring to ventilation type and location specificity. The ingress of outdoor pollution contribution in poor IAQ were also driven by other factors such as urban building orientation, the wide range of building occupancy and different set of ventilation types.

RESEARCH OUTPUTS ARISING FROM THIS THESIS

Selected oral and poster presentations:

An assessment of indoor air quality in two contrasting buildings in London ***(oral presentation)***.Analytical & Environmental Sciences Symposium, School of Biomedical Science and Health Sciences, King's College London, UK. 15th May 2011.

An assessment of indoor air quality in two contrasting buildings in London ***(oral presentation)***.MRC-HPA Postgraduate Meeting, Imperial College London, UK. 20th April 2011.

Transport of nitrogen dioxide (NO_2) and particulate matter (PM) into a mechanically ventilated office building adjacent to a busy road ***(poster)***.14th Annual UK Review Meeting on Outdoor and Indoor Air Pollution Research.Cranfield University UK. 10th – 11st May 2011.

Characteristics of particulate matter pollution inside and outside a natural ventilation school building ***(poster)***.Pharmaceutical Science Division Symposium, School of Biomedical and Health Sciences, King's College London, UK. 23rd June 2010.

Meteorological condition and building effects on indoor/outdoor (I/O) air quality in London ***(poster)***.13th Annual UK Review Meeting on Outdoor and Indoor Air Pollution Research.Cranfield University UK. 13th – 14th April 2010.

An Establishment of London Indoor Air Quality Network ***(poster)***.12th Annual UK Review Meeting on Outdoor and Indoor Air Pollution Research.Cranfield University UK. 20th – 21st April 2009.

Chapter I

Literature Review

1.1 Indoor air quality

Over the past decade, Indoor Air Quality (IAQ) has become a growing environmental issue and public health concern. Indoor microenvironments in urban buildings such as offices, schools and residences have been linked to health and comfort problems due to poor building design (Burge 1992, Burge 2004), while adverse health effects from a range of physico-chemical and biological agents have been linked to Sick Building Syndrome (SBS). Well-known agents related to IAQ include tobacco smoke, formaldehyde, asbestos, radon and *legionella* bacteria; these are commonly present indoors, as shown in Figure 1.1. Indoor air in most urban buildings also contains a mixture of organic-inorganic gaseous species and nonviable particles (Crump & Farrar 1989, Mohle et al. 2003, Petrick et al. 2011). The perception of these can be influenced by ambient components, individual building condition, and occupancy and meteorological conditions such as humidity and temperature (Burge 2004).

In the UK, people typically spend about 90% of their time indoors, where exposure to many air pollutants mainly occurs; concentrations of indoor contaminants are often higher than those found outdoors(Yu et al. 2008, Eick & Richardson 2011). The biologically relevant exposure time is seldom known, especially for mixtures as complex as those found indoors. Individual chemical species are usually found – at least when measured over a period of several hours, days, or weeks – at concentrations well below those known to cause adverse health effects. Short-term peak concentrationsare often, however orders of magnitude higher than long-term averages. Where health effects are initiated via short-term exposures– of seconds, minutes, or a few hours– especially from high peak of pollutants concentration may be of particular importance (Tucker 1991).

The sources of indoor pollutant species vary. Incremental amounts of local indoor sources are derived through indoor activities such as cooking (nitrogen oxides – NO_X), and smoking

(carbon monoxide – CO, PM, NO_X and volatile organic compounds – VOCs). Furniture, building interior surface materials (Crump et al. 2005, Jiang et al. 2010, Kang et al. 2010, Yao et al. 2011) and cleaning products (Yu & Crump 2003, Nazaroff & Weschler 2004, Huang et al. 2011) also contribute to indoor emissions. Moreover, local source pollutants from the ambient environment, including traffic, may potentially cause increments in indoor pollutant concentration via infiltration/penetration through windows, doors or ventilation systems (Partti-Pellinen et al. 2000, Johnson et al. 2004, Eisner et al. 2009).

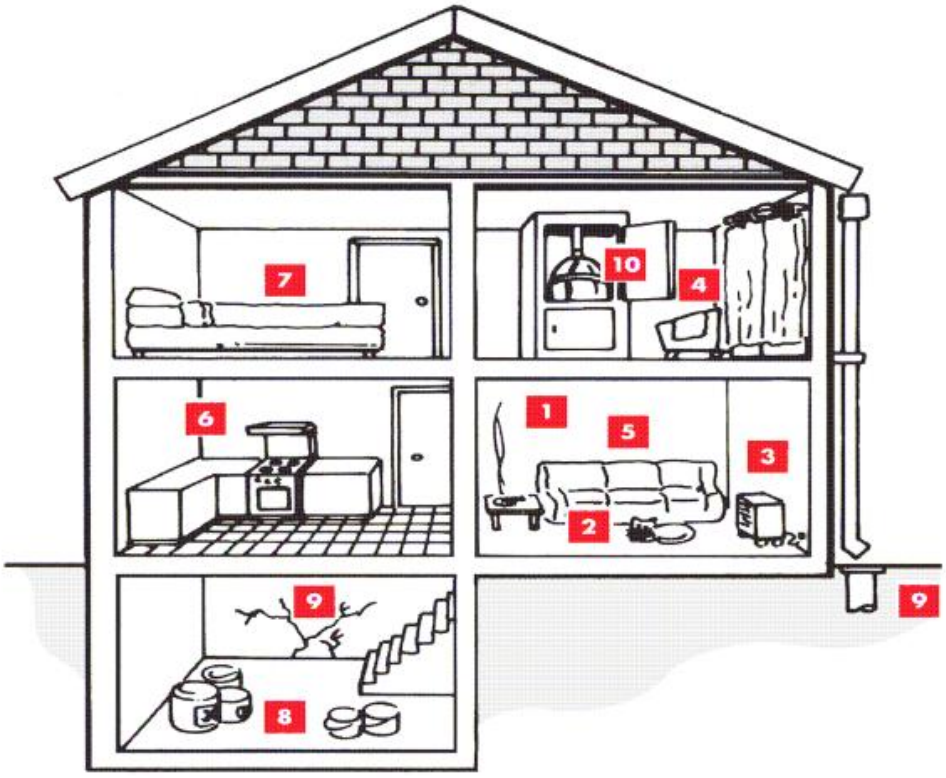


Figure 1.1: Major sources of indoor air pollution in a typical house.

Emission can occur as follows: *(1)Environmental tobacco smoke (2)Animal dusts (3)Air conditioners (4)Mould, mildew and bacteria (5)Formaldehyde (6)Cooking and heating appliances (7)House dust mites (8)Chemicals (9)Radon gas (10)Asbestos*(Carslaw 2008).

Numerous studies have proposed that indoor particulate matter (PM) and other important gaseous pollutant species (nitrogen dioxide, NO_2, and ozone, O_3) were correlated with health effects (Jie et al. 2011, Norback et al. 2011, Smedje et al. 2011, Yu et al. 2011b). In particular, PM's toxicity is well explained by its toxic components in human health (Wallace 1991, Perera et al. 2007, Reich et al. 2009). Study populations exposed to NO_2 and O_3 demonstrated increased symptoms and hospital admission cases among asthmatic children (Chauhan et al. 2003).

Although recent trends of outdoor pollutants are well documented, a lack of information on similar trends indoors persists. Consequently, at present, evidence that indoor pollutants are detrimental to health is still questionable and unknown (Carslaw et al. 2009). A recent global guideline for indoor air quality published by the World Health Organisation (WHO), 'First WHO Indoor Air Quality Guidelines: selected pollutants' (WHO, 2010), presents information on the health effects of chemical indoor pollutant exposure. The majority of the information related to individual pollutants' characteristics and guidelines is based on permitted values set by the WHO; selected pollutants include benzene, CO, formaldehyde, naphthalene, NO_2, polycyclic aromatic hydrocarbons (PAHs), radon, trichloroethylene and tetrachloroethylene. In the UK, various outdoor guidelines (EPAQS and WHO) and occupational health standards (NIOSH) were considered as a starting point for a standard comparison of IAQ. However, a common indoor pollutant such as airborne PM has not yet been effectively established. There is a clear need, therefore, to undertake research in this area to produce relevant evidence and information on a wider range of pollutant species.

1.2 Indoor air pollutant species

An estimated 1.6 million people die prematurely each year due to atmospheric pollution in building interiors, synonymous with SBS (WHO, 1990). SBS occurs either from original indoor sources or due to ingression of outdoor air pollutants, which increases indoor air pollutant concentrations. Adverse health effects such as respiratory illnesses and cardiovascular diseases were demonstrated as being associated with SBS (Katsouyanni 2003, Analitis et al. 2006, Reich et al. 2009, Breysse et al. 2010). One of the main indoor air

pollutant species is PM, which has been associated with premature death and asthmatic symptoms (Alberg et al. 2007, Reich et al. 2009). On the other hand, gaseous pollutant species such as NO_2 and O_3, which are commonly emitted from indoor combustion appliances (e.g. cooking in the kitchen) and humidifiers but alsothrough infiltration of outdoor pollutants, are believed to impose serious, non-fatal health impacts through induced oxidative stress in human lungs (Jie et al. 2011, Yu et al. 2011a).

The health implications of exposure to indoor air pollutant species are diverse, according to individual physico-chemical characteristics. In the following sections, I discuss the physico-chemical characteristics of each of the selected indoor pollutant species relevant to this project. Evidence of health effects with respect to individual pollutant species are also discussed.

1.2.1 Particulate matter

Airborne PM is composed of a complex variety of constituents including dusts, aerosols, smoke, fumes and liquid droplets. These particles vary markedly both in terms of their size and composition.In the environment, PM distribution depends on particle size, and dispersion is influenced by meteorological factors such as wind speed-direction, temperature and relative humidity;usually, fine particles will disperse freely over great distances.Indoor PM can come from cigarette smoke, degradation of VOCs, cooking, heating systems and resuspension of house settled dust. Indoor PM concentrations may be elevated due to outdoor PM contribution. Outdoor PM sources in the atmosphere can be categorised into primary and secondary particles. Primary particles are derived from natural sources (from wind-blown soil, sea spray and pollens) and anthropogenic sources (from industrial emission and motor vehicle combustion). Generally, anthropogenic sources dominate, with a greater quantity of particles in urban areas. Secondary aerosol particles are not directly emitted, but formed by reactions between atmospheric compounds; these yield sufficiently involatile products, so that partition between gas and particle phases occurs.

Even though outdoor PM is well dispersed in the atmosphere (depending on its own respective sources), a substantial proportion of outdoor PM may be transported indoors.

Outdoor particles have been shown to contribute to indoor concentrations in previous studies, e.g. via building ventilation and openings/cracks within the building shell. Examples of infiltration of outdoor PM sources include vehicular mechanical engines (gasoline and diesel powered engines), local agricultural activities (biomass combustion emissions, fugitive dust emissions and pesticide sprays) and biogenic emissions (forest fire smoke) (Nazaroff 2005, Sundell et al. 2011).

However, increments in indoor PM do not only rely on outdoor infiltration; other indoor PM sources may occur naturally or through human activity, particularly via indoor combustion at home. This includes combustion devices such as stoves and fireplaces, and activities such as cigarette smoking and candle burning (Alfheim et al. 1984, Klepeis & Nazaroff 2006). Ineffective house cleaning and improper ventilation can cause some particles to become trapped in or on a building's surfaces, such as carpet. Human movement indoors can lead to particle resuspension and deposition, which triggers asthma attacks and may cause serious respiratory problems in long-term exposures, particularly particle-gas reaction (secondary particle) such as PAHs and lead (Wallace 2001). Confirming this, recent research has shown that airborne particulate concentration in a classroom increased during its occupied period. The majority of increments in PM_{10} size was due to particle resuspension(Alshitawi & Awbi 2011).The complexity of PM elevation in indoor microenvironments can be considered in many ways, as shown in Figure 1.2.

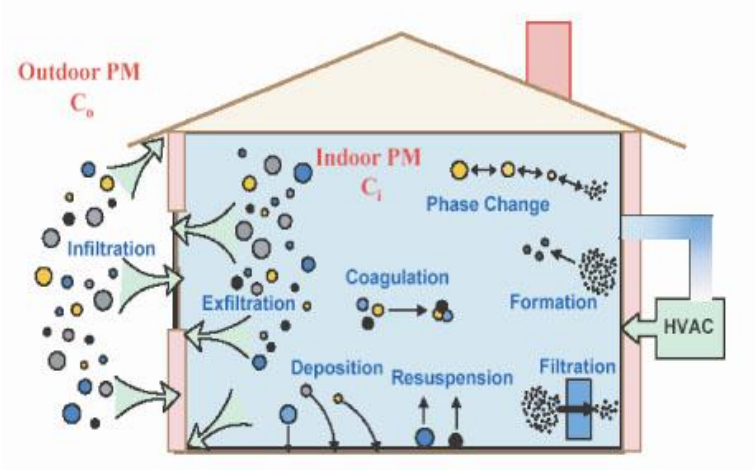


Figure 1.2: Possible indoor PM characteristics and reactions(Weschler 2004).

1.2.1.1 PM size distribution

PM size and composition are generally classified by its mode (coarse, accumulation and ultrafine PM). The particle size distribution is multimodal, as it represents a mixture of particles from different sources whose size distributions have been modified by growth processes, evaporation and removal mechanisms that favour one particle size range over another,as shown in Figure 1.3. Coarse PM particulates are classified with an aerodynamic diameter between 2.5µm and 10µm ($PM_{2.5-10}$),while accumulation mode PM refers to sizes between 0.1 and 2.5µm ($PM_{0.1-2.5}$). Ultrafine PM represents particulates with aerodynamic diameters less than 0.1µm ($PM_{0.1}$). Each type of particle sizes represents different PM sources, modes of generation and atmospheric half lives, which are described in more detail in Table 1.1.

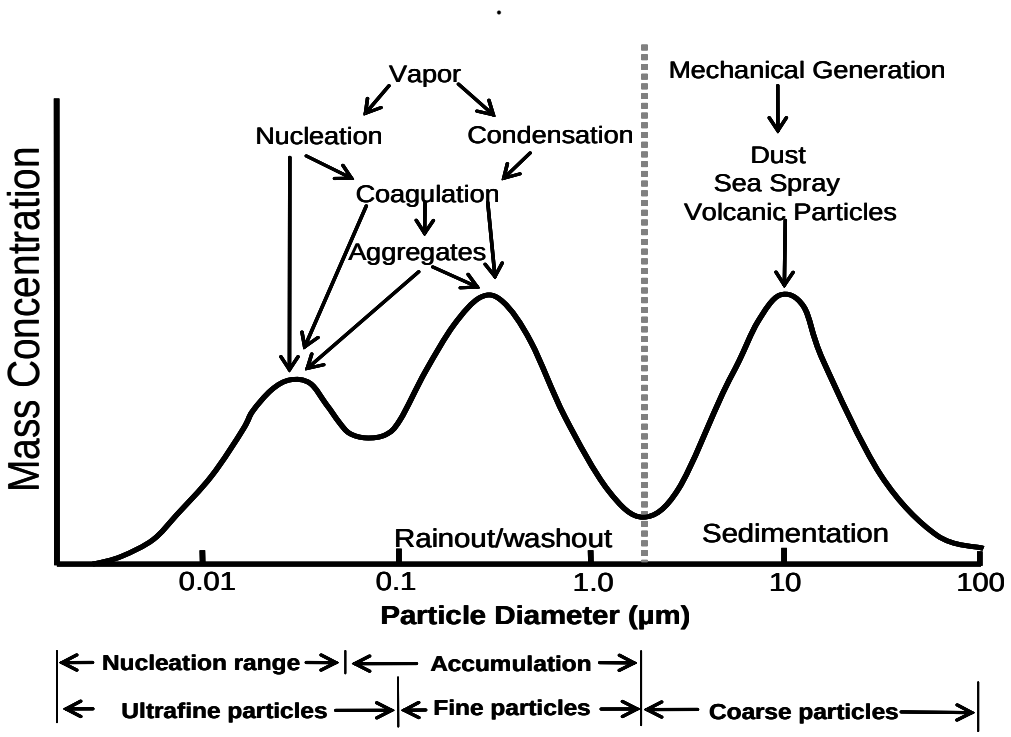


Figure 1.3: Idealised particle size distribution observable in urban environment (Seinfield and Pandis, 2006).

Table 1.1: The characterisation of particulate depending on its sizes and atmospheric sources.

Particle	Aerodynamic diameter (um)	Sources	Mode of generation	Atmospheric half life
Thoracic particles (PM_{10})	<10	-	-	-
Coarse particles ($PM_{2.5-10}$)	2.5 – 10	Outdoor: Suspension from distributed soil (farming, mining, unpaved roads) and construction. Indoor: resuspended particles from indoor surfaces, plant and animal fragments	Mechanical disruption (crushing, grinding, abrasion of surfaces), evaporation of sprays and suspension of dusts.	Minutes to hours
Fine particle ($PM_{2.5}$)	<2.5	Outdoor: Power plants, oil refineries, wildfires, tailpipe and brake emissions Indoor: Residential fuel combustion, smoking, cooking and building appliance combustion (including incense burning)	Gas-to-particle conversion by condensation, coagulation (accumulation mode)	Days to weeks
Ultrafine particle (UFP)*	<0.1	Outdoor: Fuel combustion (diesel, gasoline) and tailpipe emissions from mobile sources (motor vehicle, aircraft, ship emissions) Indoor: unknown	Fresh emissions, secondary photochemical reactions (nucleation mode)	Minutes to hours

*While the UFP size cut-off is by definition considered <0.1 µm, UFP can include particles up to 0.2µm in experimental studies using particle concentrators.This is because the distinction between the ultrafine and the accumulation modes can vary from 0.1 to 0.2µm depending upon location and season, for reasons that include, among others, variability in the size of a particulate derived from 'fresh' emission sources, and deviation from a spherical shape. (Adapted from U.S EPA and Araujo et al. 2009).

1.2.1.2 PM composition

As well as particle size, particle composition also varies markedly. The complex mixtures of PM composition are dependent on source origin and emission. Individual chemicals and elements include metals, organic and elemental carbon, VOCs, PAHs, as well as sulphate, nitrate, chloride and ammonium. Much research has been undertaken to rectify those elements in the toxicity exposure of the particle.

Organic and inorganic PM

PM organic, also known as carbonaceous species, can be categorised into two groups: elemental carbon (mainly from combustion and primary PM), and organic carbon, represented

as multiple mixture compounds with other precursor gases (e.g. PAHs). The majority of biological components, such as endotoxin in bacteria and fungi, are termed airborne PM organic. It has been shown that this type of particle is one of the major contributors to indoor odour problems in SBS (Burge 2004). A study by Chen and colleagues (2009) shows that indoor PM organic contains endotoxin formed in the outer membrane portion of gram-negative. Additionally, in most of the fungi, 1-3-β-D-glucan formed as glucose polymers in the cell walls.

PM inorganic is described bysecondary aerosol particle formation. The gas-to-particle transformation involves three major components in ambient or indoor air: sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and ammonium (NH_3). The aerosol conversion mechanism translates these components as ammonium sulphate, nitrate, chloride and sulphuric acid. The atmospheric formation process begins with the emission of SO_2 from the burning of coal and oil in stationary and mobile sources. NH_3 is the only alkaline gas of any significance found in the atmosphere. It is emitted mainly from agriculture through the spreading and disposal of animal wastes and the use of nitrogeneous fertilizers. Atmospheric ammonia is taken up on the surface of sulphuric acid droplets and particles created by the gas-to-particle conversion processes(Lee et al. 1999, Derwent et al. 2009). A recent study by Fromme et al. (2008) discovered that about 43% of $PM_{2.5}$ and 24% of PM_{10} contains sulphate, nitrate and ammonium. Indoor and outdoor ratios of these chemical compositions demonstrated that the majority of chemical compositions were of ambient origin.

PM metal composition

Metal PM can be derived directly or indirectly from ambient combustion activity – fossil fuels used in power generation, industry and automobile engines. Many studies have shownthat high concentrations of transition metals such as Fe, Mn, Ni, Pb and Zn can be found indoors associated with ambient PM, particularly from anthropogenic sources (Dermentzoglou et al. 2003, Samara & Voutsa 2005). The presence of platinum group metals in PM (Pt, Pd, Rd, Ru, Ir and Os) also indicates traffic as a possible significant contributor to the metal content of PM in urban areas, due to their use in catalytic converters(Ravindra et al. 2008).

In indoor microenvironments, PM metal elements can vary dramatically depending on indoor emission and resuspension sources. For example, PM metal elements such as Fe, Si, Mg as well as Ti and P were discovered from indoor resuspended particles due to building occupancy (Gemenetzis et al. 2006). In addition, exposure to smoking in indoor settings also contributed to indoor metal PM, such as Cl, Br, Zn and K (Landsberger & Wu 1995, Chrysikou & Samara 2009, Salmasi et al. 2010). Characterisation of indoor metal PM in the classroom by Stranger et al. (2008) revealed that high concentrations of Ca indoors was probably attributed to chalk (mainly $CaSO_4$) used on the blackboards.

1.2.1.3 Evidence of indoor PM sources and emissions

Indoor PM concentration is diverse, and depends on emissions and individual sources. Recently, much consideration has been given to examining and characterising indoor PM in different types of indoor microenvironments. Indoor combustion was believed to be one of the main contributors of indoor PM elevation, such as smoking, cooking and heating systems.

A domestic wood burning study (for natural heating during winter) in Sweden found that indoor PAH concentration during winter time in homeswith a wood-burning appliance was significantly higher than outdoors and than those without wood-burning appliances. The study found that the median indoor benz(a)anthracene (PAH species) in the wood-burning homes was 5 times higher than the Swedish health-based guideline of 0.1 ng/m^3, which also exceeded outdoors for all days of exposure (median 0.37 ng/m^3) (Johannesson et al. 2007). In addition, (Tian et al. 2008), in an investigation 26 residential homes in 6 cities in China, revealed that PM_{10} concentration increment was influenced by a building's activities without any cooking combustion. The study also found that cooking combustion from coal gas emitted high concentrations of SO_2, which was 87.6% higher than natural gas. A mechanical exhaust ventilation system was useful to exhaust indoor combustion pollutant at home compared to opening a window. In India another study measured CO and $PM_{2.5}$ emission from 51 wood and natural gas users. After 8 hours of continuous monitoring, they found the arithmetic mean for daytime CO concentration and $PM_{2.5}$ was significantly higher in wood users than natural gas users (Siddiqui et al. 2009).

Cigarette smoking, also known as Environmental Tobacco Smoke (ETS) and second hand smoke, occurs indoors. The human health effects of ETS exposure are well documented (Weitzman et al. 2005, Salmasi et al. 2010, Du et al. 2011). In a recent study investigating indoor smoking exposure (Du et al. 2011), ETS tracers were detected in 23 homes where smoking was unrestricted and indoor PM concentration elevation averaged 15 μg m^{-3}.

Particles with a diameter less than 10 μm are considered as having significant health effects. Factors contributing to increased indoor PM_{10} include resuspended particles and particles deposited onto indoor building surfaces. Previous studies have shown that the majority of residential particles are resuspended due to human activity (Thatcher & Layton 1995).Alshitawi & Awbi 2011 demonstrated in detail the factors that affect increments in indoor PM in different sized fractions – the concentration of resuspended particles was linked with ventilation rates and occupancy factors. They found that indoor particles less than 1 μm were significantly higher during occupied periods, which suggested low ventilation rate as a main factor. This study also confirmed that larger particles have a strong relationship with human activities. Indeed, other types of human activities involving building appliances (house cleaning, vacuuming and cleaning furniture fabrics) also contribute to particle suspension at home (Berry et al. 2007, Layton & Beamer 2009).

Indoor PM endotoxin such as fungi, bacteria, house dust mites and pollen also contribute to indoor particle concentrations, particularlyin buildings with moisture problems. Bio allergensin outdoor air, such as pollen, can also penetrate indoor spaces. Re-entrained road dust may be a particularly important source of bio allergens in both indoor and outdoor air (Glovsky et al. 1997).

1.2.1.4 Evidence of indoor PM and health perspectives

Airborne concentrations of selective particle sizes (PM_{10} and $PM_{2.5}$) are well described as major contributors to health effects, especially among '*fragile groups*' (the elderly, pregnant women and children with asthma). Numerous epidemiological studies have been conducted in order to demonstrate the correlation between PM exposure and health effects (Katsouyanni et

al. 1996, Aga et al. 2001, Katsouyanni 2003, Analitis et al. 2006, Biette et al. 2008, Samoli et al. 2008). These epidemiological studies also support meta-analysis done by Alberg et al. (2007) to gather evidence to show a correlation between PM and lung cancer specifically. The findings of panel studies have also shown significant contributions to lung cancer risk from indoor and outdoor air pollution, although these are weak for some agents.

A multi-city study in Europe correlated airborne PM concentration with short-term daily mortality and hospital admissions (Katsouyanni et al. 2001). The authors found that their estimation supported their previous reports on the effects of ambient particles on mortality. The estimated increase in the daily number of deaths for all ages for a 10μg/m^3 increase in daily PM_{10} concentration was 0.6% [CI=0.4-0.8%]

In light of these factors, meta-analysis suggests that pollution in urban areas worldwide causes an estimated 3%, 5% and 1% of deaths attributable to cardiopulmonary disease (among adults), upper respiratory tract/lung infections, and respiratory infections (among children), respectively (Cohen et al. 2005). Two studies have been conducted to differentiate PM size fractions from health effects. One hypothesis suggests that ultrafine particles with diameters between 0.02-0.08 microns were shown to significantly predict mortality (Choi et al. 2009, Reich et al. 2009). This finding was supported by a further study which stated that ambient ultrafine concentrations were associated with daily mortality in Europe (Katsouyanni et al. 1996, Zanobetti et al. 2003, Gryparis et al. 2004). In addition, coarse particles ($PM_{10-2.5}$) were also relatively correlated with cardiovascular symptoms and respiratory disease (Pekkanen et al. 2005, Pekkanen 2006, Pope & Dockery 2006, de Hartog et al. 2010). From an epidemiological point of view, outdoor PM concentration has also shown a strong association between increased death and lung disease (Nightingale et al. 2000, Atkinson et al. 2001, Scapellato & Lotti 2007). Taking another perspective onambient PM and biomarker measurement, various studies found that smoke exposure in men and women was associated with increased alveolar macrophage uptake of biomass smoke particulates in human lungs (Nightingale et al. 2000, Fullerton et al. 2009).

Many studies including panel and meta-analysis evidence successfully demonstrated the correlation between outdoor PM with mortality and hospital admissions. However, there is

still little evidence on the health effects of indoor PM exposure. To date, only a few studies have focused on examining the differences between indoor and outdoor PM composition and the relative contribution of its individual toxicity. Although considerable consideration has been made in elucidating the toxicological mechanisms of outdoor PM toxicity, it is difficult to draw inferences between indoor and outdoor PM without focused studies,as indoor PM could be more or less toxic than outdoor PM. Moreover, the epidemiological relationships from ambient PM studies and their magnitudes should be examined when considering the potential risk from indoor PM (Parker & Woodruff 2008).

1.2.2 Indoor nitrogen dioxide

NO_2 has a characteristic pungent odour and is recognised by its reddish brown colour; it is also volatile. NO_X is the collective term for all atmospheric nitrogen oxides, mainly comprising of NO and NO_2. NO_X in ambient environments is produced from high temperature combustion processes such as vehicle engines and power plant stations. The majority of NO_X is emitted as NO and NO_2 (Carslaw et al., 2007). NO_2 exists due to a spontaneous transformation reaction from NO, which produces the dioxide when exposed to air. Transformation reactions in atmospheric environments involve available oxidants (oxygen and ozone), as shown in Equation (1.1 to 1.3). However, this reaction is much slower in indoor microenvironments.

$$N_2 + O_2 \rightarrow 2NO \qquad \textbf{Equation 1.1}$$

$$2NO + O_2 \rightarrow 2NO_2 \qquad \textbf{Equation 1.2}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad \textbf{Equation 1.3}$$

Generally, indoor NO_2 sources originate from outdoor sources, particularly from road traffic (Shi & Harrison 1997, Harrison & Collins 1998). Nevertheless, independent indoor sources also influence indoor NO_2 concentration, such as tobacco smoke, cooking combustion (gas-wood-kerosene stoves and ovens) and boilers in heating systems (Kabir & Kim 2011).

1.2.2.1 Evidence of indoor nitrogen dioxide source and emission

In indoor and outdoor environments, NO_2 exists in gaseous form. It is a strong oxidant and easily participates with other chemical reactions, including photochemical reaction sequences initiated by solarradiation-induced activation of NO_2. Indeed, determinations of indoor NO_2 sources are more robust than outdoor source in any case. Table 1.2 summarizes the influencing factors of indoor NO_2 (WHO, 2010).

Indoor sources
Fuel-burning stoves (wood, kerosene, natural gas, propane, etc.)
Fuel-burning heating systems (wood, oil, natural gas, etc.)
Tobacco use
Source characteristics
Flued/unflued sources
Presence of pilot lights
Outdoor sources (via infiltration)
Mobile sources (petrol- and diesel-powered vehicles)
Stationary sources (industrial combustion)
Resident behaviour
Stove usage (for fuel-burning appliances)
Use of heating equipment (including cooking stoves)
Dwelling and indoor environment characteristics
Dwelling size (where there are indoor sources)
Air exchange rates
Distance to roadway
Surface characteristics
Indoor humidity

Table 1.2: Factors influencing indoor NO_2 concentration (WHO, 2010).

The Air Pollution Exposure Distributions of Adult Urban Populations in Europe (EXPOLIS) study from six European cities (including UK) discovered that smoking, gas stove usage, and outdoor temperature as well as wind speed were the strongest influencing factors at home. Adjusted regression values were determined to correlate indoor pollutant concentration with

indoor factors (Lai et al. 2006). The second report (EXPOLIS II) involving seven European cities demonstrated that indoor concentrations were associated with indoor time/microenvironment/activity patterns, with similar contributions in all cities (Schweizer et al. 2007). Quackenboss et al. (1986) examined personal exposure to NO_2 in relation to outdoor sources. They found that in 350 individuals, the association between personal exposure and outdoor concentration was weakest during winter for both gas and electric stove users ($r = 0.20$ and 0.28, respectively).

In the UK, a study to investigate the relationship between activity patterns and personal exposure to NO_2 in indoor and outdoor microenvironments was undertaken in North London and Hertfordshire. In 60 subjects aged between 21-60 years, all of whom were office workers, this study found indoor NO_2 concentrations were strongly correlated with personal exposure concentrations. Gas cookers were identified as the main contributor when compared to electric stove users as well as other microenvironments, e.g. bedrooms and living rooms (Kornartit et al. 2010). Indeed, an indoor exposure modelling study revealed that mean indoor NO_2 exposure was estimated to fall within the range of 5-21 ppb without home sources, and the concentration increased to 21-27 ppb for gas cooking users. However, outdoor source penetration also contributes to indoor NO_2 concentration, from 17% to 86% (Dimitroulopoulou et al. 2001, Dimitroulopoulou et al. 2006). In addition, another study by the Building Research Establishment (BRE) in 2001 revealed that average NO_2 concentration inside kitchens was higher than in bedrooms ($n = 854$ homes) between 1997 and 1999 (Raw et al. 2004).

Indoor NO_2 concentration appears to be influenced by outdoor sources, particularly in buildings adjacent to roads with heavy traffic. It is possible that naturally ventilated building types have a bigger impact from outdoor NO_2 penetration. A study in India demonstrated that naturally ventilated school buildings have been found to be significantly correlated with PM concentrations from traffic road and construction sites (Taneja et al. 2008). Eight French schools also revealed that indoor and outdoor ratios of NO_2 concentration vary in a range from 0.88 to 1, which illustrated that the building was not efficient in filtering or removing NO_2. The researcher also hypothesised that air tightness and the building's ventilation system offered very little protection against outdoor pollution (Poupard et al. 2005). Another study in

Taiwan examined indoor-outdoor NO_2at two hospitals located in urban and rural areas. The researchers found significant differences between the hospitals; average indoor NO_2concentration was higher in urban areas compared to rural areas (54.1 ppb – urban area and 32.7 ppb – rural, $p<0.05$). Indoor NO_2 concentration in urban areas was significant positively correlated with the traffic flow ($r = 0.72$) (Chen et al. 2009).

1.2.2.2 Evidence of indoor nitrogen dioxide and health perspectives

$NO_2$is a strong oxidizing free radical which can initiate a number of destructive pathways in the human body, particularly in respiratory cell-tissue injuries (Pilotto & Douglas 1992). High doses of NO_2 exposure cause severe pulmonary edema, diffuse lung tissue inflammatory injury and lipid peroxidation (O'Neill et al. 1995, Ben-Jebria et al. 1998). An in vitro study by Halliwell et al. (1992) demonstrated that ascorbic acid, urate and protein thiol groups are depleted when plasma is exposed to NO_2. This study also found that NO_2 toxicity involves lipid peroxidation and a depletion of α-tocopherol. In another study, depletion of urate and ascorbic acid were also observed in human bronchoalveolar lavage (BAL) fluid when exposed to lower NO_2 concentration at 94 - 1880 µg m^{-3}(Kelly & Tetley 1997).

In epidemiological studies, to date, most evidence has been correlated with indoor combustion and ETS exposure. For example, a longitudinal study of infants exposed to indoor gas appliances (stove and heating systems) reported that the risk of persistent cough increased among infants living in a home with a gas stove (van Strien et al. 2004). In Poland, gas cooking activity caused several respiratory symptoms among women over 65 years of age; this study also found decreased FEV_1 values in this group (Dow et al. 1999). Gillepsie-Bernett et al. (2008) also found independent gas stove appliances were associated with respiratory symptoms, but not with other influencing indoor NO_2 sources such as gas heaters and smoking in the home. In Australia, unflued gas heating systems were the main concern of indoor NO_2 exposure among asthmatic children at school. A more recent investigation by (Marks et al. 2010) proved that unflued gas heaters were associated with increased reports of asthma symptoms in children aged 8-12; reports include wheezing in the morning, and increased cough and airway inflammation, manifested as exhaled nitric oxide (eNO). This

study has been linked to another Australian study by Pilotto et al. (2004) which only observed increased morning wheezing among asthmatic children. However, both of these studies did not show any significant differences of lung function when unflued and flued gas heaters were compared. A similar study approach using randomised controlled trials also showed similar findings (Gillespie-Bennett et al. 2008).

In the UK, a cohort study was performed among asthmatic children by using personal NO_2 samples; in line with personal exposure, viral culture assessment and severity of asthmatic problems were recorded. The end results indicated indoor NO_2 was associated with more severe illnesses and increased virus-related asthma morbidity (Linaker et al. 2001, Chauhan et al. 2003). This study also suggested that long-term NO_2 exposure may lead to chronic cough incidences and decreased lung function.

From a human genetics perspective, several studies have shown the deleterious effects of indoor NO_2 exposure on glutathione S-transferase P1 gene (GSTP1). Savela et al. (1997) and Nakajima et al. (1995) confirmed GSTP1 encodes major phase II xenobiotic metabolizing enzymes involved in antioxidant defences to protect against oxidative stress, but with high concentrations of NO_2 can cause severe problems due to these aspects. Another related genetic study sought to determine cognitive and neurobehavioral effects of NO_2 exposure (gas appliance in house) among preschool children. This study showed that indoor NO_2 gas appliances were inversely associated with cognitive outcomes and inattention symptoms (neurobehavioral parameter). This finding also showed the strong association between the deleterious effects on GSTP1 Val-105 from indoor NO_2 gas appliances. Long-term indoor NO_2 exposure may result in the destruction of brain development among children through the first 4 years, particularly amongst genetically susceptible children(Morales et al. 2009).

1.2.3 Ozone

In the atmosphere, O_3 is not directly emitted by primary sources. It is formed through a series of reactions driven by the energy transferred to molecules during solar light radiation. Most of the formation contributors are oxidant species, such as NO_2 and non-methane volatile organic compounds (VOCs), particularly unsaturated VOCs, which react as the precursor (Johnson et

al. 2004). VOCs are more reactive than methane, their compositions are much higher in certain locations, especially from rice fields and farm animals. In the ocean and remote land areas, increments of O_3 in the atmosphere are due to photochemical reactions involving methane concentration from about 30 µg $m^{-3}$to 75µg m^{-3}. Outdoor O_3 concentration also depends on several factors such as sunshine intensity, atmospheric convection, the height of the thermal inversion layer and concentrations of NO and VOCs (specified as ratio NO: VOCs). Normally, the VOCs: NO ratio favourable to ozone formation must lie in the range 4:1 to 10:1(Prasad et al. 1990).

In rural areas, O_3 productiondepends on the availability of nitrogen oxides and varies between seasons. During summer,quarterly mean O_3 is typically highest and previous studies have shown a day-to-day association between O_3concentration and summer time (Satsangi et al. 2004). During summer, O_3 formation occurs primarily because of increased ultraviolet radiation, high temperature and low wind speed with stagnant conditions. Further, the O_3 concentration is influenced by the presence of other precursor emissions including NO from the soils and VOCs from natural sources. An estimated 15% of NO is present in summer time and may account for a larger proportion in the same area (Prasad et al. 1990).

1.2.3.1 Evidence of indoor ozone source and emissions

In ambient environments, NO and NO_2 are the major gaseous species in the production and destruction of O_3. In indoor microenvironments with insufficient UV light for O_3 generation, the majority of O_3 existing indoors was attributed to outdoor penetration via windows, opening doors or ventilation systems (Zuraimi et al. 2007, Weschler 2011). Two studies in residential areas from multiple locations in California and New Jersey demonstrated that indoor O_3 varied with similar patterns of outdoor concentration (Zhang & Lioy 1994). These studies also suggested that elevation of indoor O_3 significantly correlated with air exchange rates at home. Due to the rapid reaction of O_3 (sun light radiation), indoor O_3 is particularly prevalent during the summer season; a school study in Belgium revealed that seasonal ambience influenced NO_2 and O_3 inside the classroom. However, due to differences of deposition velocities and decomposition rates in indoor air, indoor-outdoor ratios of the gases decreased in the sequence NO_2, SO_2 and O_3(Stranger et al. 2009).

Commonly, O_3 generators that were marketed as air purifiers and photocopiers have been found to produce hazardous concentrations of indoor O_3(Oakland et al. 2001, Black & Is 2006). Evidence of O_3 emission from different dry-process photocopiers demonstrated the increment of O_3 concentration between routine machine maintenance. This study found that O_3 emission reduction was improved after maintenance, which was 16-131 µg per copy before and only 1-4 µg per copy after (Leovic et al. 1996). In addition, photocopiers and printers were also identified as emitting ultrafine particles (Kagi et al. 2007, Wensing et al. 2008, Kowalska & Zajusz-Zubek 2010). A recent study by (Saraga et al. 2011) examined the difference in indoor emissions in several microenvironments (museum, printer industry and an office). Influencing factors such as existing equipment, the number of occupants, ventilation and outdoor background were taken into consideration. The study found that a printer industry has the highest concentration of indoor emission, including $PM_{2.5}$ (151 µg m^{-3}), benzene (69.4 µg m^{-3}), toluene (147 µg m^{-3}), SO_2 (47 µg m^{-3}) and NO_2 (96.6 µg m^{-3}).Low levels of ozone were present in the printer industry and the museum (urban area),while relatively higher levels were found in offices (suburban area), indicating its outdoor origin.

Due to the rapid chemical transformation of indoor O_3, a field study was undertaken to investigate the role of classroom activities in transforming indoor pollutants into secondary organic aerosols (Morawska et al. 2009). The investigation was conducted in three classrooms under two conditions: the normal operating condition of the classroom and controlled experiments. This study found that the highest increases of indoor concentrations exceeded outdoor concentrations, as well as during cleaning activities, when detergents were used. In the controlled experiment, however, monoterpene emitted from the detergent reacted with outdoor O_3 (ranged 0.06 to 0.08 ppm) to form secondary organic aerosols. The researchers also hypothesised that the use of liquid materials for art classes (painting, gluing and drawing) and detergent for cleaning may have led to the formation of secondary organic aerosols at concentrations well above the normal background concentrations. Several research groups have also investigated the formation of secondary organic aerosols in indoor microenvironments, and the rapid transformation of indoor O_3 through reaction with VOCs, particularly terpenes such as α-pinene and α-terpineol(Nazaroff & Weschler 2004, Weschler 2011). Other studies show the secondary organic aerosol substances' production along with indoor O_3 under controlled indoor experiments such as in offices and homes (Weschler 2004,

Hubbard et al. 2005, Toftum et al. 2008, Johnson et al. 2010). These studies are in agreement, showing the secondary organic aerosol production via the transformation reaction derived from indoor O_3 generators such as printers, photocopiers, air purifiers and ionization air purifiers.

1.2.3.2 Evidence of indoor O_3 and health perspectives

Exposure to O_3 with high reactivity may lead to health problems, particularly asthmatic symptoms and respiratory illnesses. The harmful effects of O_3 are explained by its potential to oxidize the antioxidant defence systems (glutathione, uric acid and ascorbate), phospholipids, proteins as well as sugars in cell membranes as shown in Figure 1.4. Indeed, oxidative stress from oxidising free radical agents in the respiratory airways is well documented elsewhere (i.e. the most recent studies such as (Brajer et al. 2011, Kim et al. 2011, Rutkowski et al. 2011).

A rat model was used to clarify this hypothesis; in a study by (Lopez et al. 2008), ultra structural alterations were identified in the foetal bronchiolar epithelium. Three separate exposure durations were applied in this study: 18, 20 and 21 days of gestation with lungs exposed to O_3. Vacuolization in cell membranes due to oxidative damage was observed at 18 days of gestation. In addition, laminar bodies in the bronchiolar lumen were present after 20 and 21 days of gestation. This situation can be possibly explained by the oxidative damage of membrane protein and lipids' generated by O_3 inhalation. On the other hand, in a yeast type cell models study, lipid modification occurred when low O_3 exposure doses (less than 0.5 mol/mg protein) were applied. Neutral lipids (sterols) and nitrogen-containing phospholipids (phosphatidylcholine, phosphatidylethanolamine, sphingomyelin)were also modified with an increase in the O_3 dose (Matus et al. 1999). In addition, several studies have shown that O_3 exposure results in human lung inflammation for both normal subjects and asthmatic patients. This pulmonary inflammation is associated with the increase of several pro-inflammatory mediators including IL8 and IL6 in broncho-alveolar lavage (BAL) fluid (Becker et al. 1989, Devlin et al. 1991, Samet et al. 1991).

In human clinical studies, a variety of research has focused on the relation between O_3 exposure and chronic cough. For instance, the effects of ambient O_3 on respiratory function and acute respiratory symptoms were assessed in 7 to 9 year old school children who were followed longitudinally at 1 to 2 week intervals over a period of 6 months at three schools in Mexico City. The maximum O_3 concentration measured exceeded the World Health Organization guideline (8 hour mean) of 80 ppb and the U.S. standard of 120 ppb in every week. In addition, logistic regression analysis estimated the relative odds of 1.7 for a child reporting a cough (Groneberg-Kloft et al. 2006).

In other studies, O_3bio-mechanisms may influence pulmonary vagal-sensory nerve fibres, suggested to be major mediators of the cough reflex. However, these may reflect the known short-term acute effects of O_3 such as pulmonary function decrements, increased airway responsiveness and airway inflammation(Ogawa et al. 1996, Kang et al. 2010). Nevertheless, a cross sectional study (low-exposure and moderately polluted region) among adolescent school children aged 7-11 years in Taiwan did not find any significant differences in rates of chronic cough (Forsberg et al. 1997). The annual mean of the 1 hour daily maximum of ozone was 46.3 ppb for the moderately polluted region, and 34.1 ppb for the low exposure region.

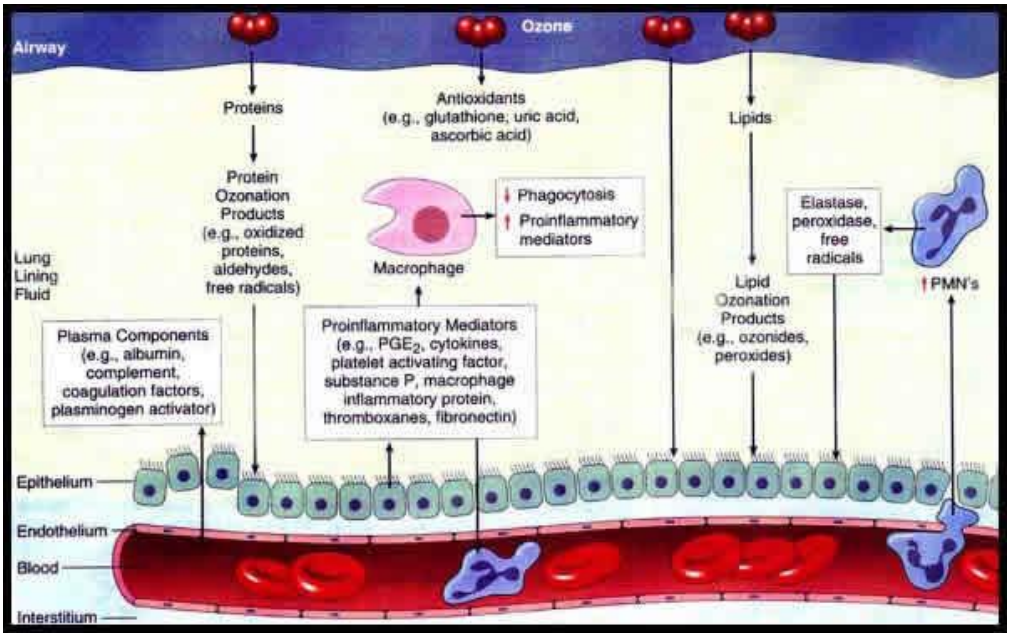


Figure 1.4: Possible mechanisms of ozone induced lung injury.

1.3 Relationship between indoor and outdoor air quality

Numerous epidemiological studies have shown the relationship between the variation of outdoor airborne pollutant concentration and changes in daily mortality as well as morbidity (Schwartz et al. 1994, Pope et al. 1995a, Pope et al. 1995b, Link & Dockery 2010). However, an ambient environment pollutant is not ideally comparable to exposure in a human community that spends most of its time indoors. Thus, consideration of both indoor and outdoor pollutant measurement in all indoor microenvironments may explain the actual concentrations to which individuals are exposed(Bekoe et al. 2011). Also, the selection of indoor microenvironments is particularly important to envisage the health risk assessments among target groups such as asthmatic children in school, and occupational hazards in offices.

To date, several studies have been undertaken to address this issue as summarised in Table 1.3a and 1.3b. The table comprises two indoor settings (school and office) from previous studies which are relevant to this project. The studies concluded that most indoor concentration was influenced by various factors, particularly from outdoor sources, building activity and indoor sources. Nevertheless, the majority of these studies determined trends in indoor and outdoor pollutant concentration based on short-term measurement campaigns. A long-term monitoring basis should ideally be considered in order to correlate changes in building use, outdoor source contribution through ventilation, as well as seasonal changes.

A recent meta-analysis study by (Chen & Zhao 2011) provides up-to-date information for both modelling and experiment (field study – residential areas and school, as well as chamber studies) on the relationship between indoor and outdoor particles. The discussion included three parameters: indoor-outdoor (I/O) ratio, infiltration factor and penetration factor. Based on previous findings, they concluded that I/O ratios varied due to the difference in size-dependent indoor PM emission rates, air exchange rates and penetration through geometry of the cracks in building envelopes. In another meta-analysis review on PM in elementary school classrooms, however, I/O PM ratios fluctuated relatively depending on school conditions and building use. The reviews summarised all the issues which might influence indoor and outdoor PM concentration, shownin the list below (Lin & Peng 2010):

a. Insufficient ventilation in schools (particularly in winter); inadequate room sizes
b. A large number of children who are more susceptible to air pollutants
c. Active classroom activity with constant resuspension of particles from room surfaces
d. Urban elementary schools being usually surrounded by major traffic lanes
e. Various indoor classroom activities and possible hazardous materials (cleaning by detergents and bleach, painting and gluing in art classes).

In addition, IAQ and ventilation are the most concerning health issues among school children. Using previous studies, (Daisey et al. 2003) revealed each of the potentially hazardous indoor pollutant species in school children. The information gathered in this study strongly indicates that inadequate ventilation in classrooms can possibly lead to health-symptom.

Table 1.3a: Summary of studies of I/O relationship undertaken in school (by years).

Exposure Details					Results			Reference
I/O pollutant species	**Site descriptions**	**Period of study**	**Instrument used**	**Seasonal comparison**	**Indoor/ outdoor concentrations**	**I/O Output**	**Seasonal output**	
PM_{10}, $PM_{2.5}$ & PM_1	University classroom in Reading, UK (mixed mode ventilation system)	3-weeks	Grimm Portable Aerosol Spectrometer	2-weeks (winter) & 1-week (spring)	Varies according to building occupancy	I/O increased during occupied period Resuspension of larger particles was observed during occupied period. Fine particles are influenced strongly by outdoor particles.	Yes	Alshitawi & Awbi 2011
CO_2, CO, NO_2 , VOCs, Carbonyls and meteorological conditions (relative humidity & temperature)	14 elementary schools in Lisbon, Portugal	Spring season only (May-June 2009)	CO_2, Relative Humidity & Temperature, VOCs (Automatic Portable IAQ Probe, NO_2 (Diffusion tubes)	Spring	I/O NO_2 ranged: 0.36 – 0.95	Indoor concentrations of CO_2 in the three main schools indicated inadequate classroom air exchange rates. At the three main schools, the total bacterial and fungal colony-forming units (CFU) in both indoor and outdoor air were above the advised maximum value of 500 CFU/m^3 defined by Portuguese legislation. The aromatic compounds benzene, toluene, ethylbenzene and xylenes, followed by ethers, alcohols and terpenes, were usually the most abundant classes of VOCs.	Yes	Pegas et al. 2011

Exposure Details					Results			Reference
I/O pollutant species	**Site descriptions**	**Period of study**	**Instrument used**	**Seasonal comparison**	**Indoor/ outdoor concentrations**	**I/O Output**	**Seasonal output**	
PM_{10}, $PM_{2.5}$ & PM_1	A classroom in an urban area in India (naturally ventilated school)	17 weeks (winter and non-winter season)	Grimm	Yes	I/O ratio analysed with ACH	Predicted indoor PM_{10} concentrations show poor correlations with observed indoor PM_{10} concentrations (R^2 = 0.028 for weekdays, and 0.47 for weekends). $NVIAQM_{bm10}$ shows the tendency to under-predict indoor [PM_{10}] during weekdays as it does not take into account the occupant's activities and their effects on indoor concentrations during class hours. Intense occupantactivities cause resuspension or delayed deposition of PM_{10}.	Yes	Goyal & Khare 2011
PM_{10}, $PM_{2.5}$, PM_1& CO_2	4 schools (naturally ventilated) in India	Winter (December 2007 – January 2008) & Summer (April – May 2008)	Grimm	Yes	I/O ratios were found to be >1 at all sites (roadside and urban areas)	During winter, mean indoor PM_{10}, $PM_{2.5}$ and $PM_{1.0}$ concentrations ranged up to 497, 220 and 135 μgm^{-3}, which were 3, 3 and 2 times lower, respectively, in summer as compared to winter. Poor correlations at all the sites except at one school located in a residential area. Inter-particulate ratios in the indoor environments were also obtained, indicating that strong correlations exist in both campaigns, which were significant at $p<0.01$.	Yes	Habil & Taneja 2011

Exposure Details					Results			Reference
I/O pollutant species	**Site descriptions**	**Period of study**	**Instrument used**	**Seasonal comparison**	**Indoor/ outdoor concentrations**	**I/O Output**	**Seasonal output**	
PM_{10}& $PM_{2.5}$	School gyms in Prague, Czech Republic (naturally ventilated)	November 2005 – August 2006	Cascade impactor	No	Not available	The indoor concentrations of $PM_{2.5}$ recorded inthe gym exceeded the WHO recommended 24-hour limit of 25 μg m^{-3}in 50% of the days measured. Theaverage 24-h concentrations of $PM_{2.5}$ (24.03 μg m^{-3}) in the studied school room did not differ much fromthose obtained from the nearest fixed site monitor (25.47 μg m^{-3}), and the indoor and ambientconcentrations were closely correlated (correlation coefficient, 0.91), suggesting a high outdoor-to-indoorpenetration rate. The coarse indoor fraction concentration ($PM_{2.5–10}$) was associated with the number ofexercising pupils (correlation coefficient 0.77), indicating that human activity is its main source.	Not available	Branis & Safranek 2011
$PM_{0.3-5.0}$	Typical classroom (naturally ventilated systems)	November-December 2005	Met One model GT-521 optical counter number	No	$PM_{0.3-5.0}$ μm: ranged between 1.2 – 4.1x105 particle/m^3	Indoor particles were observed to exhibit temporal variation patternssimilar to outdoor particles. High outdoor particle loading and high ventilation air exchange rates were thought to be predominant causes.	Not available	Tippayawong et al. 2009

Exposure Details					Results			Reference
I/O pollutant species	**Site descriptions**	**Period of study**	**Instrument used**	**Seasonal comparison**	**Indoor/ outdoor concentrations**	**I/O Output**	**Seasonal output**	
CO, CO_2, PM_{10}, Total Bacteria Count (TBC), Total VOCs & Formaldehyde	55 schools in Korea (naturally ventilated)	July-December 2004	NDIR, MiniVol Samplers, Biotest Air Sampler, Tenax-TA tubes & DNPH-coated silica gel cartridge	Yes	Yes	The problems causing indoor air pollution at the schools were chemicals emitted by building materials or furnishings, and insufficient ventilation rates. The *I*/*O* ratio for HCHO was 6.32 during the autumn, and the indoor HCHO concentrations (mean = 0.16 ppm) in schools constructed within 1 year were significantly higher than the Korean Indoor Air Standard, indicating that schools have indoor sources of HCHO.	Yes	Yang et al. 2009
PN & $PM_{2.5}$	A school near low levels of local traffic Queensland, Australia (mechanically ventilated)	2-weeks (4 September – 20 September 2006	Scanning Mobility Particle Sizer (SMPS) & Condensation Particle Counter (CPC)	No	$PM_{2.5}$ ratio (I/O ratio; $r = -0.49$, $p < 0.01$)	Correlation analysis indicated that the outdoor $PM_{2.5}$ was inversely correlated with the indoor to outdoor $PM_{2.5}$ ratio ($r = -0.49$, $p < 0.01$), while the indoor PN had a weak correlation with the I/O ratio for PN ($r = 0.34$, $p < 0.01$). Temporal variations of outdoor $PM_{2.5}$ and PN concentrations occasionally showed extremely high peaks, mainly due to human activities. The indoor $PM_{2.5}$ level was mainly affected by the outdoor $PM_{2.5}$ ($r = 0.68$, $p < 0.01$), whereas the indoor PN concentration had some association with outdoor PN values ($r = 0.66$, $p < 0.01$) even though the indoor PN concentration was occasionally influenced by indoor sources.	No	Guo et al. 2008

Exposure Details					Results			Reference
I/O pollutant species	**Site descriptions**	**Period of study**	**Instrument used**	**Seasonal comparison**	**Indoor/ outdoor concentrations**	**I/O Output**	**Seasonal output**	
PN & $PM_{2.5}$	An elementary classroom in Salt Lake City, UT, USA	25 January – 28 February 2006	TEOM & Grimm	No	I/O $PM_{2.5}$: averaged 0.12, I/O PN < 1 um: averaged 0.13	When building was occupied the indoor coarse particle count was much higher than ambient concentrations. Staying inside a mechanically ventilated building reduces exposure to outdoor submicron particles.	No	Parker & Woodruff 2008
PM_{10}, $PM_{2.5}$, CO_2 and meteorological condition (temperature & relative humidity)	68 schools in Munich, Germany	Winter (2004-2005), Summer (2005)	Laser Aerosol Spectrometer (LAS)	Yes	Not available	Indoor CO_2: 1603 ppm (winter) & 405 ppm (summer). Winter: 19.8 μgm^{-3} ($PM_{2.5}$) and 91.5 μgm^{-3}(PM_{10}). Summer PM concentrations were significantly reduced (median $PM_{2.5}$ = 12.7 μgm^{-3}, median PM_{10} = 64.9 μgm^{-3}). $PM_{2.5}$ concentrations were in generalhigher (median in winter: 36.7 μgm^{-3}, median in summer: 20.2 μgm^{-3}). In explorative analysis, researchers identified a significant increase of LAS measured $PM_{2.5}$ by 1.7 μgm^{-3}per increase in humidity by 10%. During the winter period, the associations were stronger regarding class level, reversed regarding humidity (a decrease by 6.4 μgm^{-3} per increase in 10% humidity) and absent regarding CO_2 indoor concentration.	Yes	Fromme et al. 2007

Exposure Details					Results			Reference
I/O pollutant species	**Site descriptions**	**Period of study**	**Instrument used**	**Seasonal comparison**	**Indoor/ outdoor concentrations**	**I/O Output**	**Seasonal output**	
PM_{10}& CO_2	2 primary schools in Frankfurt, Germany (mechanically ventilated)	3 weeks (February – March 2006)	DUSTTRAK & Grimm	No	Only indoor measurements involved. Data analyses according to cleaning and ventilation	Levels of PM_{10} in the classrooms during the 3 weeks were 69±19 $\mu gm^{-3}$and they were dominated by occupancy and the persons' activity. Intensified cleaning showed a significant decrease in all classrooms (79±22 to 64±15 μgm^{-3}). The effect of ventilation on levels of PM_{10} was inconsistent – levels of CO_2 were very high in all schools and could be diminished by intensified ventilation (mean 1459 to 1051 ppm).	No	Heudorf 2007
PM_{10}, $PM_{2.5}$, CO_2 and meteorological condition (temperature & relative humidity)	68 schools in Munich, Germany	Winter (2004-2005), Summer (2005)	Laser Aerosol Spectrometer (LAS)	Yes	Not available	Indoor CO_2: 1603 ppm (winter) & 405 ppm (summer). Winter: 19.8 μgm^{-3} ($PM_{2.5}$) and 91.5 μgm^{-3}(PM_{10}). Summer PM concentrations were significantly reduced (median $PM_{2.5}$ = 12.7 μgm^{-3}, median PM_{10} = 64.9 μgm^{-3}). $PM_{2.5}$ concentrations were in generalhigher (median in winter: 36.7 μgm^{-3}, median in summer: 20.2 μgm^{-3}). In explorative analysis, researchers identified a significant increase of LAS measured $PM_{2.5}$ by 1.7 µgm-3 per increase in humidity by 10%. During the winter period, the associations were stronger regarding class level, reversed regarding humidity (a decrease by 6.4 mgm_3 per increase in 10% humidity) and absent regarding CO_2 indoor concentration.	Yes	Fromme et al. 2007

Exposure Details					Results			Reference
I/O pollutant species	**Site descriptions**	**Period of study**	**Instrument used**	**Seasonal comparison**	**Indoor/ outdoor concentrations**	**I/O Output**	**Seasonal output**	
PM, NOx and O_3	8 school buildings (mixture of naturally and mechanically ventilated systems)	2-weeks	PM: GRIMM, NOx and O_3: AC31M	No	$PM_{0.3-0.4}$: 1.7 – 11.7 μgm^{-3}, $PM_{1.6-20}$: 11.3 – 61.5 μgm^{-3}	Comprehensive measurement compared previous findings (Blandeau et al. 2004). Determination of I/O ratio concluded by the building itself (flooring, window opened), outdoor environment concentration and building occupancy.	Not available	Poupard et al. 2005
O_3, NOx& PM (0.3 – 20 µm)	8 school buildings (mixture of naturally and mechanically ventilated systems)	2-weeks	PM: GRIMM, NOx and O_3: AC31M	No	Statistical analyses and PM output: $PM_{0.3-0.4}$: 1.7 – 11.7 μgm^{-3}, $PM_{1.6-20}$: 11.3 – 61.5 μgm^{-3}	The main conclusions arising from the study are: (1) the influence of the room occupancy on the particle concentrations indoors changes with different particle sizes; (2) the building's air-tightness and the outdoor concentration levels greatly influence the indoor/outdoor (*I*/*O*) concentration ratios of ozone; (3) indoor ozone and particle concentrations are negatively correlated, which may be the result of complex homogeneous and/or heterogeneous processes.	No	Blandeau et al. 2005

Exposure Details					Results			Reference
I/O pollutant species	**Site descriptions**	**Period of study**	**Instrument used**	**Seasonal comparison**	**Indoor/ outdoor concentrations**	**I/O Output**	**Seasonal output**	
PM_{10}, $PM_{2.5}$ & PM_1	University classrooms in Prague, Czech Republic (naturally ventilated)	8 October - 11 November 2001	Harvard Impactor	No	Yes	The highest 12-h mean, median, and maximum (42.3, 43.0, and 76.2 μg m^{-3}, respectively) indoor concentrations were recorded on workdays during the daytime for PM_{10}. The statistically significant (r=0.68, P<0.0009) correlation between the number of students per hour per day and the indoor coarse fraction calculated as $PM_{10-2.5}$ during daytime on workdays indicates that the presence of people is an important source of coarse particles indoors. On workdays, the daytime PM_{10} indoor/outdoor ratio was positively associated (r=0.93) with an increasing indoor coarse fraction ($PM_{10-2.5}$), also indicating that an important portion of indoor PM_{10} had its source inside the classroom.	No	Branis et al. 2005
PM, NOx and O_3	8 school buildings (mixture of naturally and mechanically ventilated systems)	2-weeks	PM: GRIMM, NOx and O_3: AC31M	No	$PM_{0.3-0.4}$: 1.7 – 11.7 μgm^{-3}, $PM_{1.6-20}$: 11.3 – 61.5 μgm^{-3}	In the absence of indoor sources, ratios of I/O NO_2 ranged from 0.88 – 1.0, which means buildings are not efficient in filtering or removing NO_2 molecules. Building's air-tightness gave very little protection against outdoor pollution.	Not available	Blandeau et al. 2004

Exposure Details					Results			Reference
I/O pollutant species	**Site descriptions**	**Period of study**	**Instrument used**	**Seasonal comparison**	**Indoor/ outdoor concentrations**	**I/O Output**	**Seasonal output**	
PM_{10}, CO_2, SO_2, NO, NO_2, Formaldehyde, Total bacterial count and meteorological condition (temperature and relative humidity)	5 schools located in residential, industrial and rural areas in Hong Kong (naturally ventilated)	Not available	Q-TRAK (CO_2), TSI DUSTTRAK (PM) and Thermo Chemiluminescent NO_X analyser (NO & NO_2)	No	The I/O average PM10 concentrations exceeded the Hong Kongstandards, and the maximum indoor PM_{10} level was even at 472mg/m^3.	Air cleaners could be used in classrooms to reduce the high PM_{10} concentration. Indoor CO_2 concentrations often exceeded1,000 ml/l indicating inadequate ventilation. Lowering theoccupancy and increasing breaks between classes could alleviatethe high CO_2 concentrations. Though the maximum indoor CO_2level reached 5,900 ml/l during class at one of the sites, CO_2 concentrationswere still at levels that pose no health threats.	Not available	Lee & Chang 1999

Table 1.3b: Summary of studies of I/O relationship undertaken in commercial buildings including offices (by years).

Exposure Details					Results			Reference
I/O pollutant species	**Site descriptions**	**Period of study**	**Instrument used**	**Seasonal comparison**	**Indoor/ outdoor concentrations**	**I/O Output**	**Seasonal output**	
PM_{10}, $PM_{2.5}$ & PM_1	Office building in urban area in Belgium	3 March – 9 May 2008	MS&T (PM) sampler and Dual channel portable aethalometers (carbon black)	No	During daytime, mass concentrations were in the ranges: 11–29, 8.1–24, and 6.6–18 μg m^{-3}, with averages of 20 ± 1, 15.0 ± 0.9, and 11.0 ± 0.8 μg m^{-3}, respectively.	At night, mass concentrations were found to be significantly lower for all fractions. Indoor PM_1 concentrations exceeded the corresponding outdoor levels during office hours and were thought to be elevated by office printers. Particles with diameters between 1 and 2.5 μm and 2.5 and 10 μm were mainly associated with soil dust elements and were clearly subjected to distinct periods of settling/resuspension. Indoor carbon black concentrations were sometimes as high as 22 μg m^{-3} and were strongly correlated with outdoor traffic conditions.	No	Horeman et al. 2010
PM, CO, CO_2, VOCs, relative humidity & temperature	Office building in urban area in Kuala Lumpur, Malaysia (mechanically ventilated)	April – September 2008	TSI Trak, Q-Trak	No	Only indoor concentrations were measured	The temperature levels and CO_2 concentrations were major factors contributing to SBS complaints among office workers. Indoor pollutants in old buildings were high, while new buildings showed high temperature indoor pollutants and ultrafine particles.	No	Syazwan et al. 2009

Exposure Details					Results			Reference
I/O pollutant species	**Site descriptions**	**Period of study**	**Instrument used**	**Seasonal comparison**	**Indoor/ outdoor concentrations**	**I/O Output**	**Seasonal output**	
PM_{10}, O_3& CO	Mixed building compartment (office & classroom) in suburban area in Greece	June 2004 – February 2005	NDIR (CO), UV absorption (O_3), Beta Adsorption Monitor (PM_{10})	No	Yes	I/O PM_{10} is higher during occupied period. Indoor PM_{10} was lower during holiday period. Indoor O_3 and CO were found in low levels. Indoor PM_{10} concentration showed good correlation with O_3 (r=0.45) and high correlation with CO (r=0.98).	No	Triantafyllou et al. 2008
PM in different size fraction	Non-domestic building in Leipzig, Germany (naturally ventilated)	Summer 1999 and winter 2000/2001	DMA & CPC	Yes	I/O correlation analysis: larger particles sizes (> I um) exhibit rather linear concentration decrease.	In the absence of significant indoor sources, the number of indoor concentrations of particles is clearly lower than the outdoor concentrations.	Yes	Wolkoff et al. 2003
PM_{10}, $PM_{2.5}$ & PM_1 as well as wind direction/wind speed	Non-domestic building adjacent to a busy road in London (mechanically [MV] & naturally ventilated [NV])	April – October 1998	NDIR CO monitor, TEOM	No	I/O ratio mean with wind direction: CO: varied 50-60%; PM varied 20-30%. I/O in NV spaces depended on the distribution of wind direction.	I/O ratios for the whole period were generally lower in the NV compared to MV spaces. The I/O ratio in one NV space changed by a factor of three between theearly stages and final stages of monitoring, with a ‘‘stable’’ final value (±5%) achieved after 0900 h of monitoring. In the MV spaces under constant fan speed, constant values for the I/O ratio were achieved for CO within 4 hof the start of monitoring.	No	Ni Riain et al. 2003

1.4 Building ventilation, IAQ and environment

Ambient air quality in urban cities in industrialised countries has improved enormously in recent decades. However, during this same period, IAQ has declined due to improper urban building designs, energy conservation and also the complexity of new building materials and indoor pollutant sources (Olesen et al. 2006, Olesen et al. 2011). Today, an acceptable IAQ in most urban buildings is mainly defined by specifying good ventilation design and condition. Ambient air quality in urban areas is usually at its highest concentration and IAQ inside buildings draws from ambient air, there will always be major issues designing urban buildings with regard to ventilation (Kukadia et al. 1996, Kukadia & Palmer 1998). In urban locations, building orientation as well as the surrounding structures and shapes are important determinants in the building contamination process (Mfula et al. 2004).

In theory, proper ventilation helps improve IAQ. Ventilation can control indoor humidity, and contribute to indoor air cleaning via effective dilution and removal processes. Further, the proper design, operation and maintenance of the ventilation systems are essential in providing indoor air that is free of harmful concentrations of pollutants. The USEPA website suggests that increasing the rate at which outdoor air is supplied to the building decreases indoor air problems. Furthermore, buildings with high ventilation rates may suffer indoor air problems due to uneven distribution of air, or insufficient exhaust ventilation (USEPA Fact Sheet, 1990).

Urban ventilation building systems are commonly categorised into three different ventilation modes:

a. Natural

Natural ventilation is the process of supplying and removing air through indoor space by using the flow of external air and indoor space conditions such as temperature and pressure differences. It is controlled by either wind driven ventilation (wind) or stack ventilation (temperature variation). Typically, air movement within building envelopes is determined by opening doors and windows; air exchange rates provide the proportion of internal and external air inside buildings.

This system is relatively inexpensive, requires minimal maintenance and zero energy consumption. However, minimal treatment of incoming air is one of the crucial disadvantages.

b. Mechanical

This type of ventilation system is also categorised as spot and dilution ventilation. Spot ventilation draws air from a particular location (i.e. bathroom and kitchen) and expels the internal pollutants outside the building. Normally, it involves exhaust fan installation and is controlled by timers and/or electric switches or de-humidistat detectors. Dilution ventilation addresses the entire living space. This type of ventilation is typically applied in most buildings in urban areas, particularly offices. Heating, ventilation and air-conditioning (HVAC) systems are commonly used. However, they are rarely designed to reduce common external gaseous air pollutants at their typical concentrations. This type of ventilation system has high operating and maintenance costs, and requires high energy consumption and carbon dioxide emissions.

In addition, the most concerning issues with this type of ventilation is the building supply and exhaust locations – air supply vents installed too close to building exhaust vents re-introduce contaminated exhaust air into the building, increasing indoor pollution.

c. Mixed-mode

This ventilation type is also known as hybrid ventilation. Figure 1.5 shows an example. This system attempts to apply the benefits of both natural and mechanical ventilation. It is controlled by a combination of operable windows (either manually or automatically) and mechanical systems (HVAC systems). The integration between both ventilation systems is practical and maximises comfort. This strategy also avoids the significant energy costs of year-round air conditioning.

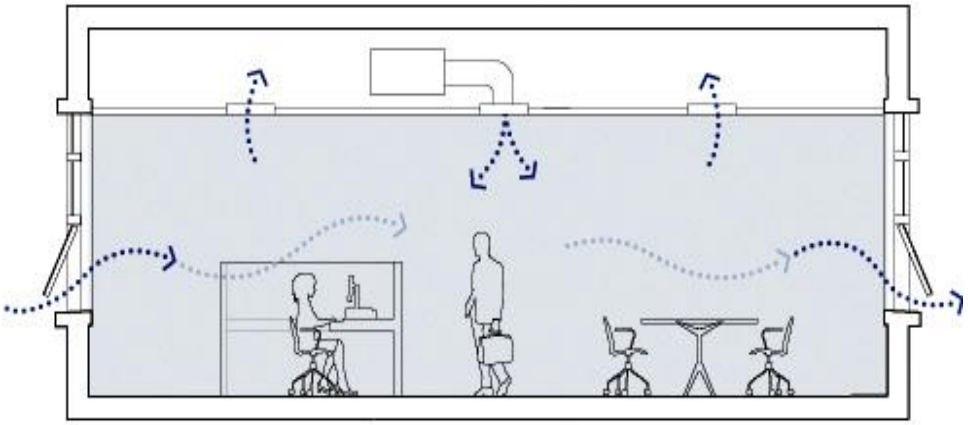


Figure 1.5: Mixed-mode ventilation (Brager, 2005).

However, in the interest of mechanical ventilation system into variable air volume system instead of constant volume system – there are four possible combinations of natural and mechanical systems (Chadderton 2007):

a. ***Natural inlet and outlet (NI – NO):***maximizing the adventitious of openable windows, louvers, chimneys and doorways. No energy is needed to provide the ventilation air. However, these depend upon prevailing winds strength and direction and the effect of rising warm air currents.

b. ***Natural inlet, mechanical outlet (NI – MO):***mainly in dwellings, offices, factories or public buildings. The usage of mechanical extract fans in space wall and roof as ducted systems where the air to be discharged away from the occupied space owing to its contamination with heat, fumes, smoke, water vapour or odour. This system can may caused slight reduction in air static pressure is caused within the building, and external air flows inwards. This inflow is facilitated by air inlet grilles, sometimes situated behind radiators or convectors heater. There is no filtration of incoming impurities. This system is used particularly for toilet or kitchen extraction, smoke removal from public rooms and heat or fume removal from industrial premises. Heating of the incoming air is essential for winter use.

c. ***Mechanical inlet, natural outlet (MI – NO):*** the usage of fan convector or ducted system to allow air blown into the building, in order to pressurise the internal microenvironment setting slightly with a heated air supply. This system is used particularly for offices, factories, large public halls or underground boiler plant rooms through adventitious openings and permanent air bricks or louvers.

d. Mechanical inlet and outlet (MI – MO): full usage of mechanical control of air movement. Normally the used of single-duct system is used particularly for sealed building from the external environment.

1.4.1 Building ventilation and street canyon effects

A high density of buildings and increasing number of vehicles on the streets leads to a high density of emitted air pollutants in urban areas. As a result, urban dwellers tend to be amongst both the major sources and sufferers of pollutants (Hall et al. 1998). Since significant quantity of urban pollutants from vehicle combustion sources enter urban buildings, pollutant dispersion in street canyons is particularly important. The term street canyon refers to a relatively narrow street between tall buildings, which line up continuously along both sides (Nicholson 1975). Therefore, this type of building orientation is thought to have high pollution impacts due to automobile source emissions (Huang et al. 2000).

In general, air pollutants flow and dispersion in a street canyon is determined by local meteorological conditions (wind speed and direction) and street canyon geometry. Normally, the form of the canyon geometry consists combination of horizontal and vertical surfaces which acts as the walls and the street is the ground. However forasymmetric canyons is involved when the certain buildings has a different height than the other opposite building. Furthermore, studies within urban street canyon must take into account the height, length and width of the canyon. There are two perspectives measurement (aspect ratio and sky view factor) to consider in order envisaging the impact of air pollution within urban street canyon:

a. ***Aspect ratio:*** or height/width ratio of the average height of the building (on both sides) to the width of the street.
b. ***Sky view factor:*** ranges from zero to one; calculated as the amount of sky visibility from the ground up. The lower sky view factor, the canyons retain more heat during sunny day and creating a higher heat release at night.

A number of wind tunnel studies (Roney & White 2010, Saha et al. 2011) and other dispersion models studies (Dabberdt et al. 1973, Manning et al. 2000, Bady et al. 2011, Yassin 2011) were investigated in order to understand dispersion characteristics. Most of these studies agree with each other and draw similar conclusions on the impact of pollutant source discharge and sensitive receptors.

Briefly, Figure 1.6 shows the typical observation when roof-level wind blows within about $\pm 60^{o}$ of the cross-street direction – the pollutant dispersion under this scenario develops a helical circulation in the street. At street level, the cross-street pollutant component is opposite the roof-level wind direction, causing a down flow of relatively clean air in front of the downwind buildings that face the roof-level wind, and an up flow across the street. This theory is important to describe the pollutant dispersion at one site in this study (mechanically ventilated office building at roadside site). As part of analysing this theory, the wind blow distribution is applied in order to understand the dispersion characteristics within building envelopes (opening doors at main entrances) driven by local meteorological conditions (wind speed and direction).

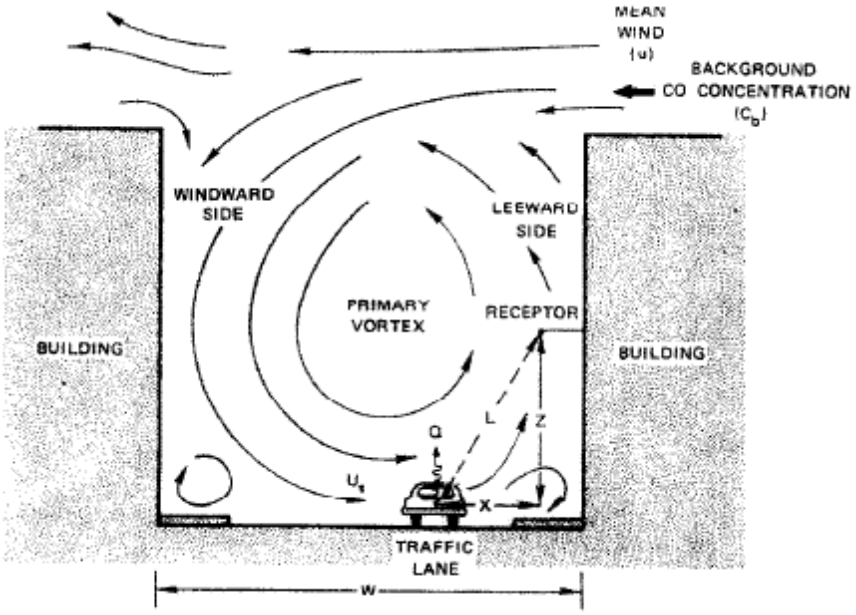


Figure 1.6: Schematic of flow pattern in a street canyon (Dabberdt et al. 1973).

The dispersion of pollutants in urban areas affecting indoor environments is robust and relatively complex, depending on many factors, such as:

a. Nature of pollutants, topography of the location and distance of its source from the building;
b. Building characteristics (ventilation) and occupancy;
c. Building orientation due to its size, shape and surrounding structures;
d. The movement and the density of vehicle combustion within the street canyon.

1.5 Indoor air pollutants and respiratory tract lining fluid (RTLF)

Generally, from a physiological perspective, O_2 and CO_2 exchange mechanisms occur in alveoli at the lower respiratory tracts, including airborne particulate and oxidative gaseous pollutant species such as O_3 and NO_2. The toxic capacity of oxidants through oxidative stress has been related to lung injury, as it is the first point of entry in respiratory inhalation, particularly in human RTLF. In addition, PM depositions through inhalation in the respiratory tracts vary due to particle size. As shown in Figure 1.7, the smaller the particle, the more PM will be deposited.

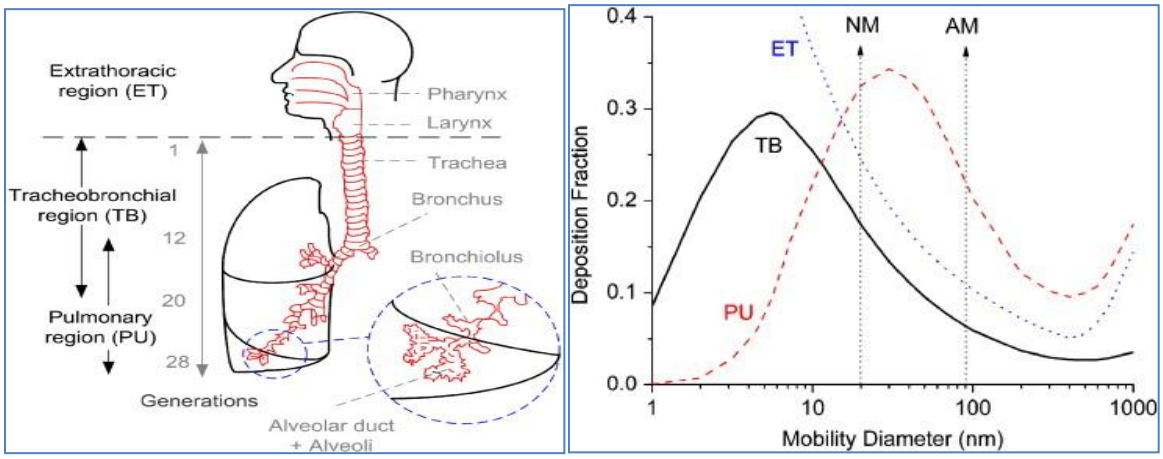


Figure 1.7: Schematic representation of the human respiratory tract (left). Calculated deposition fraction of inhaled particles as a function of particle diameter for the three regions of the human respiratory system: extrathoracic (ET), tracheobronchial (TB), and pulmonary (PU). The arrows indicate a characteristic nucleation (NM, mass median) and accumulation (AM, surface area median) mode particle diameter (right) (Adapted from Alfoldy et al. 2009).

RTLF in human lungs has two layer-compartments containing a lower aqueous sol phase and upper mucus, gel-phase that overlays the surface of the respiratory epithelium. The first physical defence against inhaled oxidant toxins is considered to be the RTLF that covers the respiratory epithelium from nasal mucosa to alveoli. In spite of protein, lipids and carbohydrates, the complex human RTLF contains a range of antioxidants. These include a non-enzymatic antioxidant with low molecular weight antioxidants (ascorbate, urate and glutathione), as well as enzymatic antioxidants (superoxide dismutase, glutathione

peroxidase, catalase, and metal binding proteins) (Cross et al. 1994, van der Vliet & Cross 2000, Schock et al. 2004).

Oxidative stress through ROS production has been related to the capacity of oxidants to cause injury in the lung. Induced oxidative stress mechanisms occur in a biological matrix to produce ROS and have been associated with secondary generations of reactive oxygen, such as singlet oxygen, superoxide radical, peroxyl radical, hydroxyl radical, hydrogen peroxide and nitrogen species (van der Vliet et al. 1999).

Several studies have shown that pollutant oxidants have a strong association against antioxidant scavengers in the human RTLF defence system. Oxidative gases, such as O_3, are identified as causing rapid depletion of both urate and ascorbate in human plasma after 4 or 6 hour incubation with 16 ppm O_3(Cross et al. 1992). Consequently, another study also revealed that reactive absorption of O_3 by plasma urate and ascorbate was found to be more efficient at low O_3 concentrations at 2 ppm. The study also found a loss of plasma-SH correlated with increment of O_3 concentration exposure. The researchers suggested that protein-SH groups such as mucin and glutathione may serve as important scavengers of O_3(O'Neill et al. 1995). Indeed, O_3 exposure was also demonstrated in other studies as causing urate depletion in human nasal lavage (Mudway et al. 1996, Housley et al. 2002).

Furthermore, a rat model study by Ben-Jebria et al. (1998) demonstrated protein oxidation with respect to NO_2 concentration in both bronchoalveolar lavage fluids (BALF) and in buffered albumin solutions. The protein depletion rate was much lower in BALF when compared to albumin solutions, and possibly explained the role of antioxidants in BALF-protected proteins from being oxidized by NO_2. In another study by Kelly & Tetley (1997), ascorbate and urate were depleted significantly in a synthetic RTLF model when exposed to NO_2 concentration ranged between 50 – 1000 ppb.

In addition, recent studies have highlighted ascorbate depletion in the PM dose-dependent pattern; (Mudway et al. 2004) demonstrated ascorbate depletion in the synthetic RTLF model by diesel exhaust PM. Another study found evidence showing that ascorbate was

depleted in a near-linear fashion over time by the three different black carbon particles. The study also found the ascorbate depletion rate varied depending on carbon particle types, as well as the presence of metal chelators(Zielinski et al. 1999). However, this study did not observe any significant depletion in urate within the same RTLF exposure model. In another study to support these findings, biomass derived particles were used to examine the effect on synthetic RTLF model. They found similar depletion patterns, which meant significant ascorbate loss after 4 hours incubation with dung cake resuspended particles. The antioxidant losses were inhibited in the presence of metal chelators, suggesting that biomass derived particle have considerable oxidative activity, largely attributable to their transition metal content (Mudway et al. 2005).

However, to date, there is still limited information with regards to indoor pollutant oxidants in human RTLF, particularly for indoor airborne PM. The consistent findings from previous studies may not explain the actual pollutant exposure concentrations to which individuals are exposed. Therefore, there is a clear need to gain information and better understand the relationship that exists between indoor and outdoor pollutants' oxidative toxicity.

1.6 PhD aims and objectives

PhD overview

My PhD study overview is to provide a better understanding of the impact of outdoor pollution sources on indoor microenvironments at two contrasting building type and location within London. The buildings to be used are office and school environments, rather than residential, with little or no domestic cooking.

PhD aims and justifications

This will achieved by determination of the two distinct aims:

a. The essential component of my PhD project will involve the long term monitoring of PM (PM_{10} and $PM_{2.5}$) and gaseous pollutants (NO_X, NO_2 and O_3) at each of the campaign buildings. By producing measurements over a long time period, the transfer of pollutants over a wide ranges of meteorological and seasonal conditions can be established which is not possible with short-term regimes. The resulting database will allow differences caused by changes in building use, methods of natural ventilation and heating/cooling cycles of mechanical ventilation to be investigated.

b. The development of long term monitoring indoor/outdoor pollutants database will involve the analysis of PM captured from indoor/outdoor sample filters to assess sample toxicity. The novel assessment will be based on the capacity of PM filter suspensions to deplete lung-physiologically relevant antioxidants from a synthetic model of human respiratory tract lining fluid (RTLF). Published literature has shown clear temporal and spatial variation in ambient PM oxidative activity throughout Europe. The nature of particulate matter changes markedly inside building due to the shift in sources and location. Therefore, it will be more informative to study particulate metrics other than mass, which obscure any changes in sources on the transfer of pollutants into a building.

PhD objectives:

a. The development of long-term monitoring of gaseous pollutant (NO_X, NO_2 and O_3) and particulate matter (PM_{10} and $PM_{2.5}$) databases at adjacent internal (indoor) and external (outdoor) sampling points at each of the campaign buildings.
b. To assess the differences in indoor/outdoor pollutants concentrations caused by changes in building use (occupancy), meteorological condition (wind speed and wind direction) and seasonality at each of the campaign buildings.
c. To assess the differences in PM-induced oxidative activity between indoor and outdoor, according to the building use (occupancy), meteorological condition (wind speed and wind direction) and seasonality at each of the campaign buildings.

Chapter II

Materials, Instrumentation & Analytical Methods

2.1 Introduction

In this chapter, the methods used in indoor and outdoor pollutant monitoring, airborne PM sample collection and data analysis are discussed. This includes the novel study of determination of PM mass loading on filter papers and the methods used to characterise settled PM dust by using synthetic respiratory tract lining fluid (RTLF) exposure.PM toxicity assessment via oxidative potential analysis were based on the capacity of PM filter suspensions which were collected in weekly/bi-weekly basis for long term run – to deplete physiologically relevant antioxidants ascorbate (AA), urate (UA) and reduced glutathione (GSH) from RTLF model. The novel method used was based on novel SOPs and was refined as part of this study which will be discussed further in this chapter.

The long term continuous monitoring of indoor and outdoor pollutants was performed between August 2008 and May 2011, involving two locations in London: Walbrook Wharf, Upper Thames Street, a roadside site in central London; and Eltham, Greenwich, an urban background site in suburban London. The sites were categorised according to their building characteristics as follows:

a. Case 1 (Corporation of London, Walbrook Wharf, Upper Thames): mechanically ventilated office building.
b. Case 2 (Environmental Curricular Centre, Eltham, Greenwich): naturally ventilated school building.

2.2 Site and sampling description

Two different types of building ventilation were selected in this study, representing two typical building scenarios in London. The differences in ambient pollutant exposure

between these sites may have different impacts on building dwellers. Other factors may influence pollutant impact, such as building occupancy and activity, which were monitored in line with indoor and outdoor pollutant monitoring.

In addition, meteorological parameters were used to identify the influences of wind patterns on indoor-outdoor pollutant concentrations at both site campaigns. Due to the availability of the instrument for rental in the long term running and cost restriction for equipment's maintenance, it is possible to install individual meteorological local station at each study campaign. However, in order to optimise the effect of meteorological condition at both study sites, the use of meteorological data from a remote site at Bexley site (BX 2). BX 2 was identified in previous reports (Defra, 2011) to represent general atmospheric conditions, which derived a homogenous local source at both study sites.Nevertheless, in this specific case, particularly at roadside site, due to effect of surrounding built environment on wind speed and wind direction; this is considering as a major limitation in this study.

The following sections give brief descriptions of the two selected cases.

Figure 2.1: Map of London to describe the location of study campaigns.

2.2.1 Case 1: Environmental Curricular Centre, Eltham, London.

Site Location:

The Environmental Curricular Centre is an Environmental School situated in Eltham (suburban London) with the grid reference 543982, 174676 and latitude 51.452739242389, longitude 0.0707951708960 (Figure 2.1). The school building is surrounded by 'green' spaces such as gardens, parks and a golf course, thus making it minimally exposed to local external pollution sources. The building has one floor consisting of two classrooms, two administration offices and other common school facilities such as toilets, a pantry and a store room. The indoor pollutant measurement equipment was set up in a frequently used classroom. The room dimensions were 17m (length) by 7.2m (width) by 5m (height). The fabric of the classroom consisted of a reinforced concrete block walls with dry plastered wall and a wood-framed ceiling. The room was equipped with standard school furniture made of wooden chipboard and metal fixed to the floor. About 20 separate Polyvinyl chloride (PVC)-metal chairs were available for visitors. There was one whiteboard for colour-board markers, one overhead projector and one standing laboratory table with 2 built-in sinks on each side of the classroom wall.

Building characterisation and occupancy:

The building was open daily and the classroom was occupied 3-4 times a week. The number of students present during a teaching hour in this particular classroom varied between a few individuals and full capacity – maximum 25 students. The classroom was predominantly used for teaching and environment-related art activities such as painting, soil and insect activities, paper making, gluing and drawing by children aged 8-12 years. Therefore, a large number of bottles, plates of garden soil and liquids used for those activities were present in many locations within the classroom. The occupancy usually changed every second hour according to class schedules, along with a short 20 minute lunch break at mid-day. The presence of students was quantified by means of a personal-hour indicator, which was calculated by multiplying the number of students by the time of their presence (in hours) in the classroom (Branis et al. 2005). The average number of

student-hours per the 7-hour high occupancy period was 105 (a maximum of 210 and a minimum of 70). The building was open during school holidays with at least one or two teachers-on-duty present; however it was closed on public holidays. Building occupancy and diary activity information is detailed in Appendix A.The ideal precision f building diary activity in this particular study site should be done by visual observation, in order to monitor the individual school activity on a daily basis. However, due to time constraint and investigator commitment in the long term run, the established data of building occupancy/diary activity was taken from official attendance record monitored by school administration. This is considered to be another limitation which will add uncertainty in further analysis in this thesis.

Building Ventilation:

The classroom had one window without any ventilators and two doors – one facing the lounge administration area, and another leading to the other classroom, used mainly used as a library and as storage for animal models. The classroom's windows faced the playground outside, which featured an artificial pond garden.

Pollutant measurements:

The gaseous pollutant analysers were placed on stainless steel racks inside the store room beside the classroom. The analyser's sampling inlets were installed in both outdoor and indoor locations within 2 and 7 metres of the roof, respectively; sampling height was within 2-3 meters from ground level. For particulate matter, indoor and outdoor monitors were installed at similar ranges. These parallel sampling inlets for both pollutant parameters allowed both measurements to be monitored systematically.Analyser maintenance and calibration was undertaken every fortnight in line with London Air Quality Network (LAQN) standard protocol (LSO Manual, 2002).

Outdoor

Front view of Environmental Curricular Centre, Eltham

Outdoor grass playing field beside the classroom

Indoor

Furniture and internal condition in the classroom

Window opening onto a closed grass playing field

Figure 2.2: External and internal views, Environmental Curricular Centre, Eltham,Greenwich (Case 1).

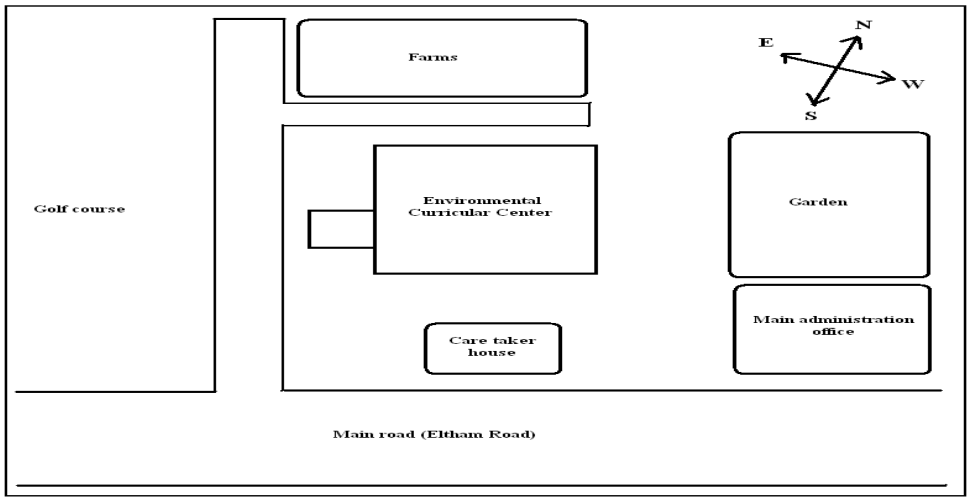


Figure 2.3: Diagram showing building orientation and surrounding area, Environmental Curricular Centre building.

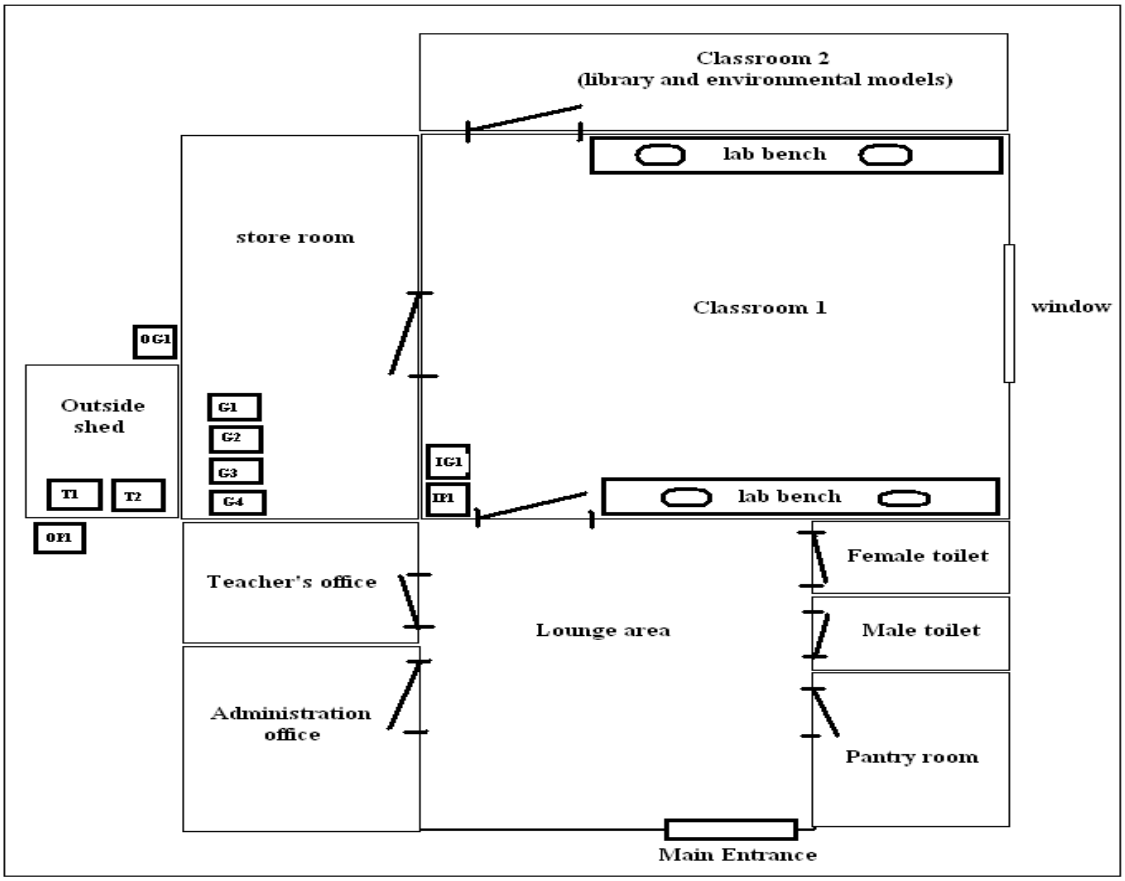


Figure 2.4: Diagramshowing sampling locations and surrounding area of the classroom, including outdoor and indoor analysers and sampling inlets, Environmental Curricular Centre.
Notes: IP1 & OP1 *(indoor & outdoor particulate dust monitor)*, **G1-G4***(outdoor & indoor ChemiluminescenceNOx& Ozone analysers)* and **OG1 & IG1***(indoor and outdoor gaseous pollutants sampling inlets).**T1 & T2** (TEOM PM_{10}& $PM_{2.5}$ which are co-located with outdoor PM OSIRIS).*

2.2.2 Case 2: Corporation of Londonbuilding at Walbrook Wharf, Central London.

Site Location:

The Corporation of London building is situated in the heart of Greater London with the grid reference532520, 180800 and latitude 51.510568732243, longitude -0.091767355160 (Figure 2.1). The building is located near Blackfriars Railway Station, off Upper Thames Street, to the north of the River Thames. This five-storey office building houses the Borough's Department of Environment and Occupational Health. The main entrance is on the ground floor, about 2.5m from the roadside. Congestion is common; at peak periods, long queues can form stretching the entire length of the street, with queuing exacerbated by traffic lights to the west. This section of Upper Thames Street has street canyon characteristics (i.e. narrow road width of approximately 20m and high building heights of about 30m).

Building characterisation and occupancy:

The indoor and outdoor pollutant concentrations were monitored within the building's main entrance reception,a 1500m^2 area. The main entrance was in normal use and without any obvious indoor pollutant sources such as printing machines; there was also a non-smoking policy on the premises. The fabric of the entrance area consisted of a reinforced concrete frame with reinforced concrete floor slabs and glass cladding. This area was staffed by at least one person on duty, and operated from 0800 until 1800 Monday to Friday, closed during non-working hours and weekends. It had acentralised high ventilation air conditioning (HVAC) system with filtration. Air-tightness in the main entrance area was affected by theautomatic entrance doors.

Building ventilation:

The mechanical ventilation and exhaust system in this building functioned at all working hours and was controlled by the central heating system. Air ducts were installed throughout the whole building to supply air via diffusers, including at the main entrance. The building's external ventilation air supply was located on its upper roof. Air

ventilation included both the exchange of external air as well as the circulation of air within the building. Formal interviews with building managers and visual observation regarding ventilation system maintenance were conducted before actual monitoring began. However, due to safety issues, the inlet located on the roof was not investigated. The ventilation system operated during working hours from 0800 until 1800 Monday-Friday, and was switched off at the weekend. The ventilation air duct filters were changed every 6 months to ensure continued good performance.

Pollutant measurements:

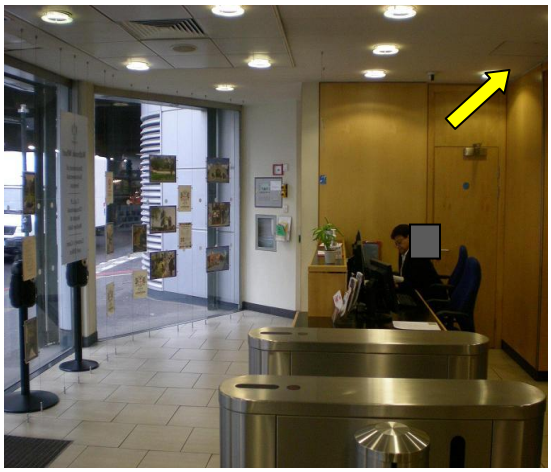
The gaseous measuring equipment was placed on a table in a small sealed room within the main entrance area. The outdoor gaseous pollutant samplinginlet was positioned approximately 3m from the kerb at a height of 2.5m above the pavement. The indoor inlet was positioned within the room at the reception area, approximately 2.5m above reception desk. An indoor PM monitor was also installed within the same area. Due to electrical supply difficulties and safety issues, a outdoor PM monitor could not be installed at this site. However, outdoor PM_{10} data was available from a London Air Quality Network (LAQN) site located about 500 metres from the study site at a similar distance from the kerb of Upper Thames Street. Due to the use of different types of particulate measurement devices indoor and outdoor at this site, inter-comparison analysis was undertaken to compare the performances of these two instruments, which is explained in the next section. Analyser maintenance and calibration was undertaken every fortnight in line with London Air Quality Network (LAQN) standard protocol (LSO Manual, 2002).

Outdoor

Entrance at ground level, 2.5m from kerbside

Automated opening doors at Corporation of London building

Indoor



Staff-on-duty at reception area (indoor gaseous pollutant sampling inlet pointed in yellow arrow)

Internal view from reception area facing street tunnel (outdoor gaseous pollutant sampling inlet pointed in yellow arrow)

Figure 2.5: External and internal views, Corporation of London building (Case 2).

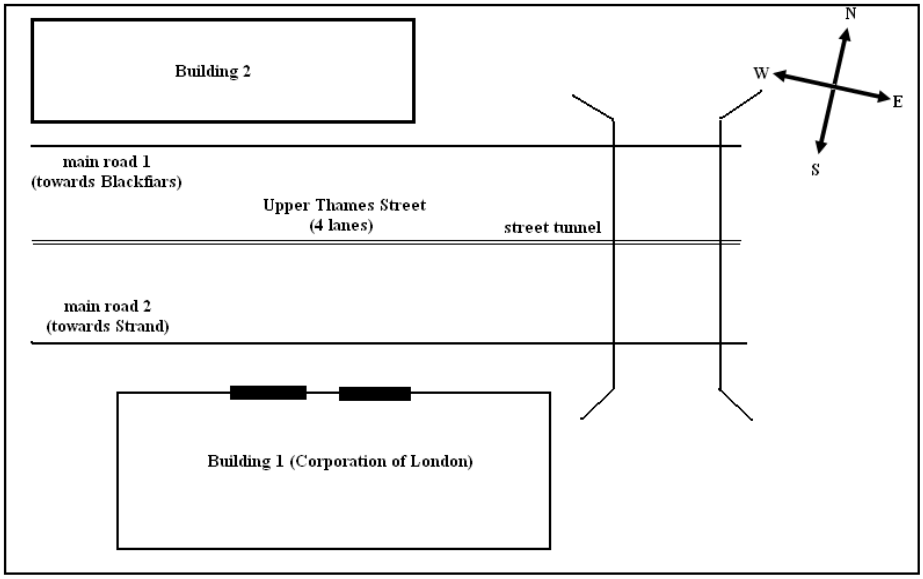


Figure 2.6: Diagram showing building orientation and surrounding area, Corporation of London building.

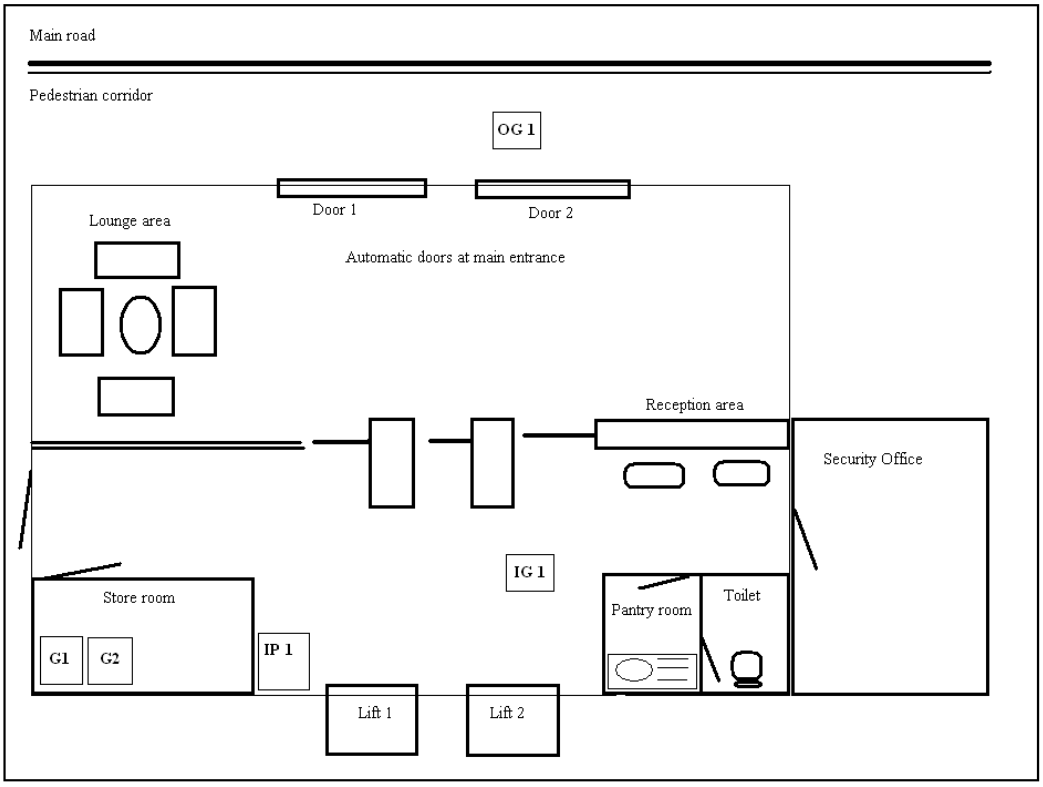


Figure 2.7: Diagram showing sampling locations and surrounding area at the main reception, including outdoor and indoor analysers and sampling inlets, Corporation of London building.
Notes: IP1 *(particulate dust monitor and indoor sampling inlet)*, **G1 & G2***(outdoor and indoor ChemiluminescenceNOx analysers)* and **OG1 & IG2***(outdoor and indoor gaseous pollutants sampling inlets).*

2.3 Instrumentation and parameters measured

The parameters measured in this study include traffic-related gaseous pollutants (NO_X, NO_2, NO and O_3) and also samples of airborne total suspended particles (TSP) with different PM selective size fractions of PM_{10} and $PM_{2.5}$. Indoor and outdoor gaseous pollutants were measured using Chemiluminescent Oxides of Nitrogen analyser (NO_X) and a UV Absorption Ozone (O_3) analyser, whereas airborne PMs data were collected using OSIRIS portable light scattering devices from Turnkey Instruments, UK. This section describes the principle of automated instrumentation used to obtain a high quality long term database of mean concentration NOx-NO_2-NO and PM measured every 15 minutes. Table 2.1 shows the instrumentation used and parameters measured at each study site.

Table 2.1: Description of sampling instruments used and parameters measured at each study site.

Study site	Instrument used	Parameters measured	Sampling inlets
Mechanically ventilated office building (Corporation of London)	Chemiluminescent Oxides of Nitrogen	*NO_X, NO_2 and NO* [a]	Indoor/outdoor
	UV Absorption Ozone	*O_3* [a]	Outdoor only
	OSIRIS Dust Monitor	*PM_{10} and $PM_{2.5}$* [b]	Indoor only
	TEOM analyser	PM_{10} [d]	Outdoor only
Naturally ventilated school building (Environmental Curricular Centre)	Chemiluminescent Oxides of Nitrogen	*NO_X, NO_2 and NO* [a]	Indoor/outdoor
	UV Absorption Ozone	*O_3* [a]	Indoor/outdoor
	OSIRIS Dust Monitor	*PM_{10} and $PM_{2.5}$* [c]	Indoor/outdoor

*Notes: [a] pollutant parameters monitored from **August 2008-June 2011**;[b] from **March 2010-March 2011;** and [c]from **March-June 2011.**[d]TEOM PM_{10} analyser was positioned 500m along road represent outdoor PM measurements, and pollutant parameter monitored from **March-June 2011.***

The two different locations were equipped with similar analysers for each pollutant species in outdoor and indoor environments. Each gaseous analyser and airborne OSIRIS Dust Monitor is describedbelow.

2.3.1 Instrument 1: Chemiluminescentoxides of nitrogen (NO_X, NO_2 and NO)

The instrument used in this study was a Model 42 manufactured by Thermo Environmental Instruments Inc., and supplied by Thermo Unicam, Cambridge.

Gaseous pollutant species (NO_X, NO_2 and NO) were measured using a chemiluminescent technique as shown in Figure 2.8. The analyser utilised photometric detection from the gas phase reaction of O_3 with NO. In this reaction, some of the resultant NO_2isproduced in an electronically excited state; this immediately decays to the ground state (or normal NO_2) while emitting light in the spectral region from about 600nm to 2400nm, with a peak at about 1200nm. The intensity of light generated in the reaction isproportional to the reactant concentration of NO, and the reaction isapplicable to the direct measurement of atmospheric concentrations of NO.

Similar measurements of NO_2 are made indirectly by chemiluminescence by first reducing the NO_2 to NO; the resultant NO then reacts with ozone and the light intensity from the reaction can be measured. In practice, NO_2 is made indirectly by chemiluminescence by first being reduced to NO using a converter. Any NO already present in the air sample passes through the converter unchanged, causing a resultant total NO_X concentration equal to NO + NO_2. A portion of the air sample also reacts with ozone without having passed through the converter, which yields the NO concentration. This latter NO measurement is subtracted from the previous NO_X measurement (NO + NO_2) to yield the final NO_2 measurement.

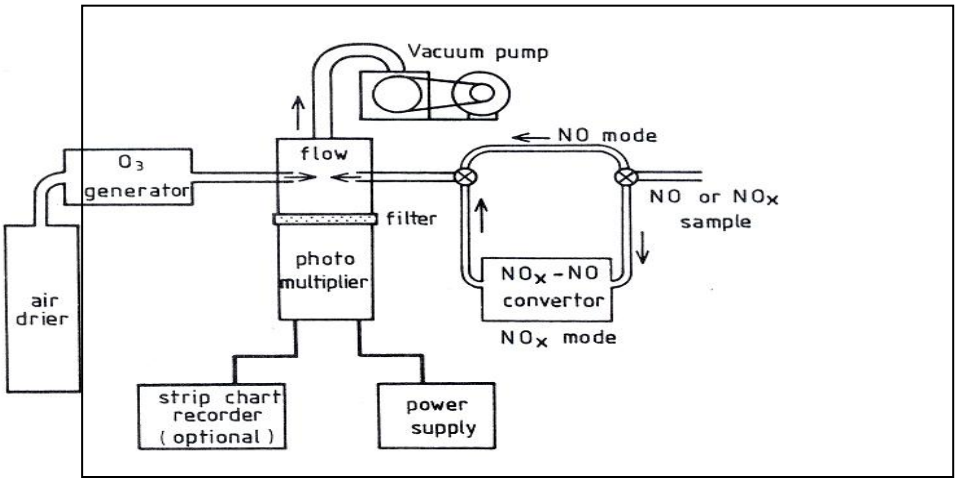


Figure 2.8: Schematic diagram of chemiluminescent analyser(Harrison et al. 1997).

2.3.2 Instrument 2: UV absorption ozone (O_3)

The instrument used in this study was Model 49, by Thermo Environmental Instruments Inc. By utilising ultraviolet absorption by ozone at wavelength 254 nanometres, the ozone concentration ismeasured by comparison with the ozone-free air sample. The principle of the Beer-Lambert Law isapplied to relate transmittance to the ozone concentration. The first absorbance cell reading isquantified as absorbance of an air sample after the catalytic conversion of ozone to oxygen, and the second absorbance isconsidered an unchanged air sample. The differences between the two readings aredue to the ozone content in the air sample, as shown in Figure 2.9.

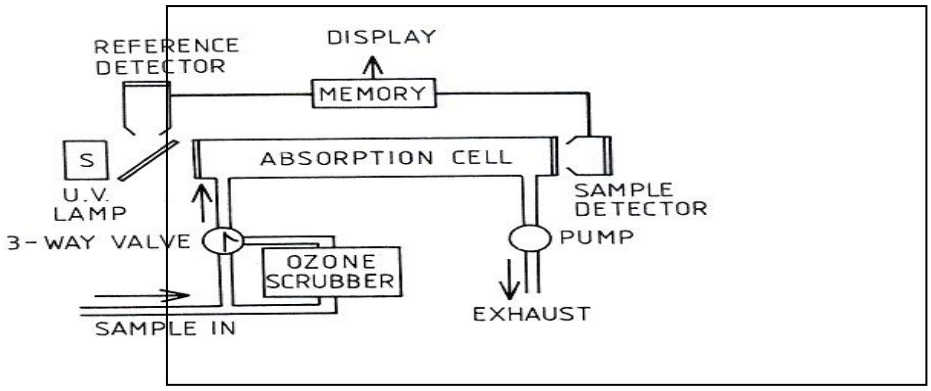


Figure 2.9: Schematic diagram of a UV photometric analyser for Ozone (Harrison et al. 1997).

2.3.3 Instrument 3: PM OSIRIS dust monitor (PM_{10} and $PM_{2.5}$)

Indoor and outdoor airborne PMs were measured using OSIRIS Dust Monitors (Turnkey Instruments), with two different sized fractions selected – PM_{10} and $PM_{2.5}$. The instruments used in this studywere on loan from the London Borough of Greenwich and Winchester Council.

By using a light scattering technique (as shown in Figure 2.10), the concentration of airborne particles and dust detected in the size range 0.4 microns to about 20 microns. All particles above 20 microns in size areconsidered as 20 microns. The instrument receives air samples by a pump with a flow rate 0.6 l min^{-1}. It has inlet heating to 50^{o}C to minimise the effects of water droplets and particle-bound water. Air samples pass through a laser beam in a photometer and through a filter to collect particle samples before reaching the pump. It measures the intensity of the light scattered by individual particles, allowing an assessment of aerodynamic diameter. Using known physical inlet collection efficiencies for different sized fractions, the photometer then assigns a percentage of the calculated mass to a size fraction, thereby simulating a physical size selective inlet. It detects light scattered by particles through 10 degrees or less, minimising the effects of reflected and refracted light and therefore the particle colour. Individual particle sizes from air samples areconverted into electrical pulses to allow direct measurements in µg m^{-3} (Turnkey Instruments, 2002).

Furthermore, particles can be collected on a Whatman GFA 25mm filter for subsequent mass determination and therefore instrument calibration. Modifications were made to change the Teflon filter to a 25mm microfiber glass (MFG) filter in order to avoid any damage to the filter during the particulate resuspension procedure for further lab analysis of oxidative potential. Filters were changed and air pump pressure calibrated every fortnight. The filter preparation and weighing procedure is discussed in the next section.

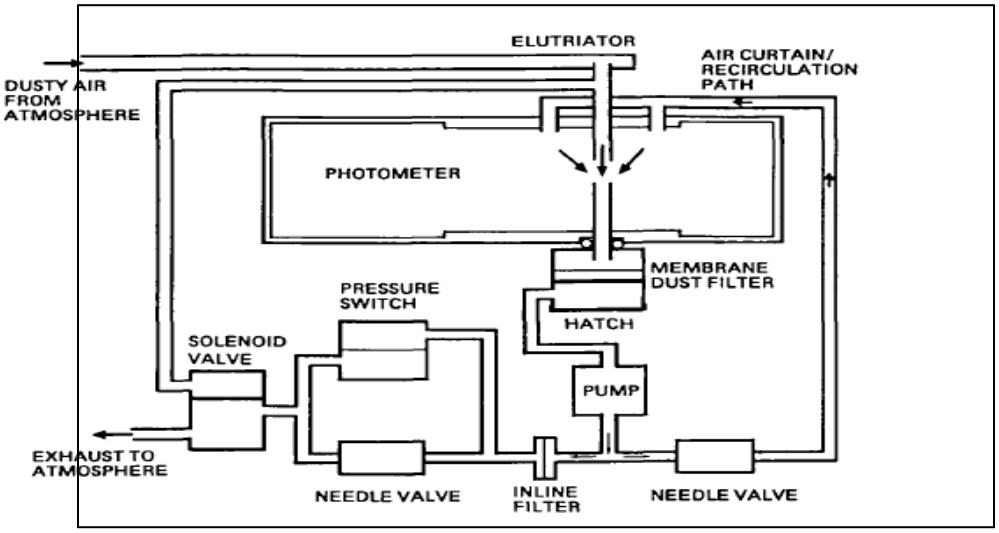


Figure 2.10: Photometric schematic diagram of OSIRIS Dust Monitor (Turnkey Instruments, 2002).

As mentioned in previous section, the available PM_{10} TEOM data was used to compare indoor PM_{10} inside the mechanically ventilated office building (Case 1) measured with the OSIRIS Dust Monitor.Briefly, the TEOM 1400 samples passed through a Rupprecht&Patashnick supplied PM_{10} inlet with a flow of 16.7 l min^{-1}, which diverted 3 l min^{-1} of the flow to a 16mm PFTE-coated glass fibre filter positioned on a tapered glass element. The sampling stream and filter were heated to 50^{o}C to maintain a stable temperature and eliminate interference from water on the filter. The mass measurements rely on the measurement of the resonant frequency of an oscillating system consisting of the filter and glass elements. The TEOM is operated as part of the AURN and benefits from extensive quality control procedures; the calibration factors and flows are checked every three months.

2.4 Analyser maintenance and data processing

All analyserswere stand-alone units that measured continuously and recorded 15-minute averages with an internal logger. Data were automatically polled and checked daily using Environment Research Group Software Monnet 2.0. Each gaseous analyser performed automatic zero and span check calibrationsdaily. On a fortnightly basis analyserswere checked, sample filters were changed, the NO_X analyser was calibrated against a UKAS accredited gas standard, and data were corrected and scaled accordingly.

On a six monthly basis the gaseous and TEOM equipment was audited by a UKAS accredited (to ISO 17025) organisation. The O_3 analyser's accuracy was determined using a National Physical Laboratory (NPL) transfer standard photometer. The NO_X analysers were tested with zero gas and span concentration mixtures, which were certified against Primary Standards held at NPL. In addition to this,gaseous and TEOMequipment was serviced at six months to protocols equivalent to those on the UK national monitoring network (AURN).The OSIRIS Dust Monitors were calibrated 8 weeks before the monitoring campaign took place in line with a master reference instrument in a calibration chamber at Turnkey's factory. The calibration was performed over a 30 minute period with an artificially generated particle stream at about 800 µg m^{-3}, periodically reduced to 0 µg m^{-3}. Agreement between instruments achieved 1%-2% of reading across each particle size fraction.

After installation, both the indoor and outdoor equipment were initially run with sampling points in the same position outside, for a period of time as a control method. Once it had been established that the data from the outdoor and indoor analyses were comparable, the sampling inlets for the indoor equipment were moved to their long-term indoor sampling locations.

At Greenwich the indoor sampling point was located in a classroom adjacent to where the equipment is installed, at a point 3mhigh and approximately 1m from the wall. Children and staff used the classroom regularly. At the Corporation of London site, the indoor

sampling point was in the entrance foyer of the local authority offices at a height of approximately 3m. The foyer was permanently staffed during office hours.

High quality data was achieved by using appropriate sampling protocols followed by a data ratification process. Raw data from these analysers were processed by Monnet 2.0; audit and service information were used to ratify data to AURN standards before differences in maximum and mean values were calculated (LAQN manual).

2.5 Data quality: Inter-comparison of particulate data

As mentioned in the previous section, two different types of particulate devices were involved in this study. The available PM_{10} TEOM data was used to compare indoor PM_{10} inside the mechanically ventilated office building measured with the OSIRIS Dust Monitor. However, these instruments were different in terms of operational characteristics and also had limitations as sample-based techniques. For these reasons, 15- minutes data inter-comparison was undertaken to compare the relationship between two particulate instruments and their sensitivity by co-locating instruments of the same make and model at a roadside monitoring site on Marylebone Road in central London over the period ofMarch until May 2011.

Generally, inter-comparison results were divided into two types of analysis:

a. Time series analysis
b. Linear regression analysis

Time series analysis

Figure 2.11 shows the 15-minute averagesof the two particulate monitors. In general, both of these instruments' measurements showed a similar pattern throughout data monitoring. However, PM_{10} concentration measured by the TEOM was higher than that measured by the OSIRIS. It was also important to point out that the over read was not

consistent at some point, and occasionally the OSIRIS measurements exceeded the TEOM's reading. The differences may be related to meteorology and PM sources.

OSIRIS VS TEOM (PM_{10}) – Marylebone Road (test site)

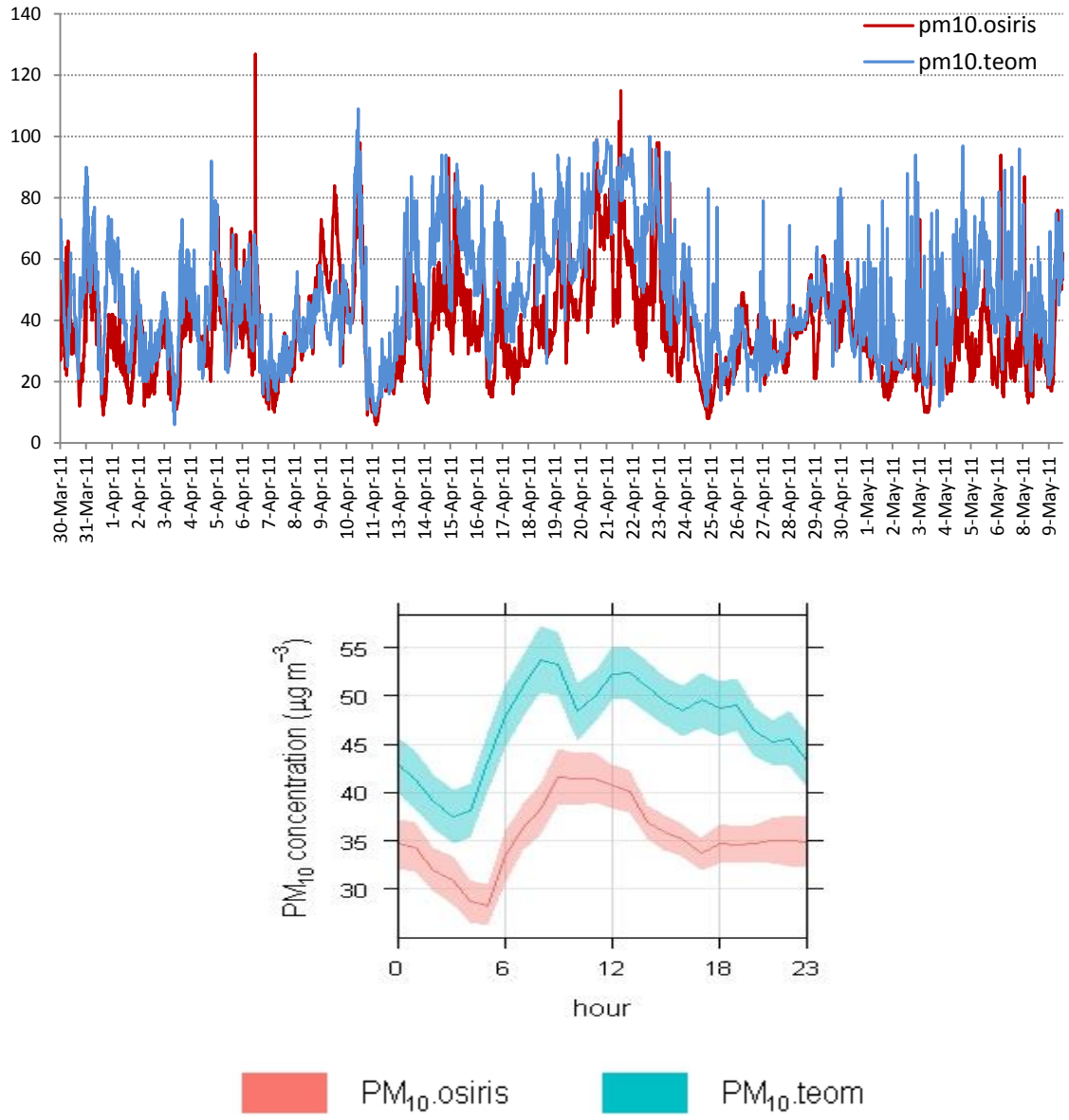


Figure 2.11: Diurnal variation inOsiris PM_{10} and TEOM PM_{10} at Marylebone Road (test site).

Linear regression analysis

Linear regression analysis yielded a relationship between the PM_{10}measurements of the two instruments (TEOM and OSIRIS) in the form $y = mx + c$, where m is the slope and b is the offset. The alternative relationship, $y = mx$, where the line of best fit is forced through the intercept, was also examined. This information can be used to provide 'correction factors'between these two instruments via m, slope correlation values. In this analysis, an independent value was determined using OSIRIS concentrations, and a dependent value using TEOM PM_{10} concentrations.

The PM_{10} measurements from previous daily average variation profiles were plotted into a scatter plot analysis to identify the regression equation value. Figure 2.12 shows the linear regression between the TEOM PM and the PM OSIRIS results undertaken at the Marylebone Road roadside site, considered a test site for the inter-comparison analysis. The results show that the agreement between these two instruments produced an R^2 of 0.41. This finding determined that the TEOM PM can explain about 41% of the variation in the OSIRIS PM_{10}. The small offset and the close agreement between the slopes of the regression lines (more than 40%) for PM_{10} indicates that this agreement holds throughout the range of concentrations.

As a result, the slope correlation obtained from Figure 2.12 as m value (0.52) was used as a 'correction factor' to recalculate the TEOM PM_{10} concentration measurements particularly at office site. Nevertheless, there are a few limitations needs to be considered before any assumptions will be discussed further in this thesis. Besides the precision location of the instruments was not installed at the front of study building – positioned 500 m along the road, the loss of percentage in agreement between these instruments may differ due to meteorology condition differences and are likely to lose the same particulate matter components from the air samples. Other confounder needs must be considered when comparing these two instruments. There are known limitations to the sample-based technique – filter handling and conditioning, for instance, can introduce errors.

OSIRISPM$_{10}$vs TEOM PM$_{10}$ – Marylebone Road (test site)

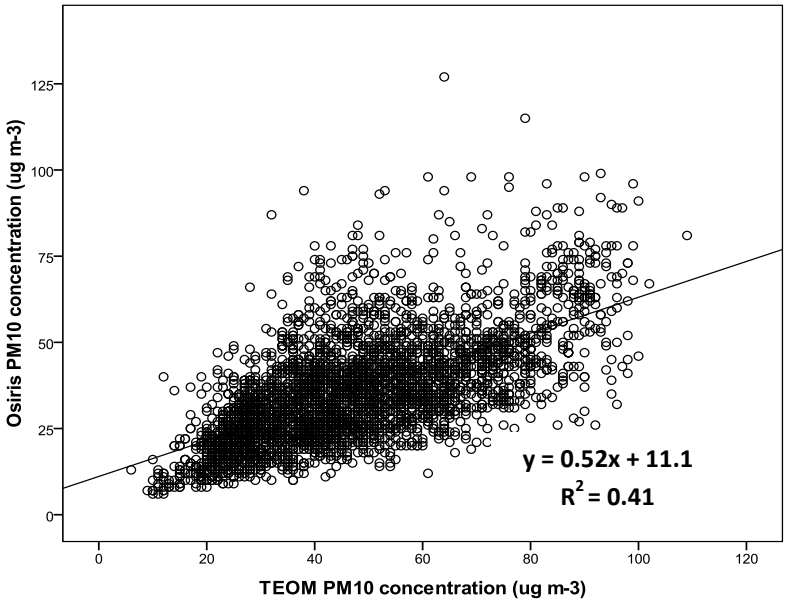


Figure 2.12: 15-minute average linear regression between OSIRIS PM$_{10}$ and TEOM PM$_{10.}$

2.6 PM filter exposure and collection

This procedure has been developed from work undertaken by the National Physical Laboratory (NPL) and reported by Brown et al. (2003) and Brown et al. (2002). Conditioning and weighing procedures were undertaken at the London Borough of Bexley facility at Sidcup.

Filter paper was conditioned in the weighing room for a minimum 48 hours before and after sampling exposure. Filter conditioning is necessary to avoid the effects of humidity on the PM mass weight measurement. A 25mm MFG filter (Whatman, US) was used for collecting sample exposures in this study, as it is suitable to avoid filter damage during PM sample resuspension under sonicator pressure for PM oxidative potential (OP) analysis. The 25mm MFG filter has high loading particle retention in liquid (µm): 1.6, with particle retention at 98% efficiency (Whatman, US). Previous studies have shown that the MFG filter did not suffer from electrostatic charging during the weighing procedure. Hence, it increased the stability of weight reading and accuracy for PM mass

before and after sampling exposure (Shilton, 2003). A Mettler-Toledo Ltd UMX2 micro-balance with a readability of 1 µg was used to weigh all filter papers; it was attached to MassAnalysis.mdb software on a computer to record every single weight value automatically. Real-time temperature, % humidity and atmospheric pressure were recorded during weighing operations.

The filter papers were placed onto a conditioning rack in the weighing room with appropriate temperature and humidity to avoid any water vapour. They were again conditioned for 48 hours using a similar procedure after sampling exposure. During the mass analysis procedure, all filter papers were weighed twice to confirm the stability of the filter weight. Weights differing by more than 55 µg were discarded. Each of the weighing sessions used different filter papers; a zero reading was measured through the control known-weight for 50mg, 200mg and blank filters. A similar MFG filter was used as a blank filter. The accuracy of weighing measurements was checked again according to repeatable weight values within ± 1 µg. Un-exposed control filters were used and applied in a similar procedure to identify any changes of mass weight due to humidity.

All filter papers containing PM exposure at each site were stored at $4^{o}C$ at the Bexley Sidcup facility's weighing room, to prevent any loss of volatile and semi-volatile species on PM filters. In order to avoid inconsistency in the accuracy of PM mass measurements, all exposed filter papers were conditioned and weighed under similar conditions with temperature and humidity consistent with the pre-sampling exposure.

2.7 PM toxicity assessment

Two major PM toxicity evaluations involving the analysis ofmetal dependant and independent oxidative activity of PM samples were derived from outdoor-indoor sources at the two studysites. Both assessments were based on the capacity of PM filter suspensions to deplete physiologically relevant antioxidants ascorbate (AA), urate (UA) and reduced glutathione (GSH) from a synthetic model of human respiratory tract lining fluid (RTLF). It worth noting that there are two filter types were involved in this analysis, PM OSIRIS micro fibre glass for non-PM size fractionated samples (TSP) and PM TEOM Teflon filter for PM_{10} samples.

Materials

All materials and chemicals were purchased from Sigma-Aldrich chemie GmbH, Riedstr, Germany or FlukaChemika, Buchs, Germany, unless otherwise stated in the following protocols.

Chelex Resin Treated Water

Water for the preparation of the antioxidant and organic stock solutions was added to 1L 18.2MΩ H_2O (ElgaPurelab Maxima System) and left to stir overnight (24 hour mixing) at room temperature. It was then filtered through a 0.45μm cellulose nitrate membrane filter and the final pH was adjusted to 7.0 using 1mMHCl. The 1mM HCl stock solution had also been similarly prepared using Chelex-treated water. All reagents were prepared in a polycarbonated beaker to avoid metal contamination from laboratory glassware.

Determination of PM Oxidative Activity

An assessment of PM oxidative potential was measured via RTLF incubation for ascorbate (AA), Urate (UA) and glutathione (GSH). These are the 3 main antioxidants in PM samplesused to identify antioxidant effects*in-vivo*. In principle, synthetic RTLF was designed to comprise 3 main biomarkers in one RTLF stock concentration (2mM) in ascorbate (AA), urate (UA) and glutathione (GSH), as mentioned above. The RTLF stock needed to be prepared and checked for a concentration of 2mM for each biomarker before any RTLF stock could be added to PM samples for RTLF exposure.

Synthetic RTLF Preparation

0.0336g of UA was added to 100ml Chelex-resin treated water; the solution was then heated on a stirring hotplate for 10 minutes, but not allowed to boil. After the uric acid had dissolved, the solution was allowed to cool to room temperature. At this point AA (0.0352g) and GSH (0.0614g) were added to achieve a final concentration of 2mM. The final pH was adjusted to 7.0 using 1mMNaOH and the volume made up to 100ml. This stock solution was stored as outlined above in 10ml aliquots.

PM Filter Extraction

Exposed fibre glass filters were placed in 50ml Falcon tubes and vortexed vigorously with 2ml methanol for about 10 minutes. PM samples were then sonicated on ice for 30 seconds at amplitude of 5 microns. Supernatant PM samples were then transferred into pre-weighed 50ml Falcon tubes for another 10 minutes of vortexing. In order to get absolute extracted PM samples, nitrogen gas was used to dry down the methanol solution with a gently warm underwater bath at 37^{o}C. Filter blanks were run in parallel with exposed PM filters using an equivalent concentration and extraction procedure. The resulting PM samples were resuspended in ultrapure Chelex-treated water at pH 7.0 to the desired concentration (between 150 and 1000µg ml^{-1} depending on the yield). Resuspended PM samples were vortexed for 2 minutes and sonicated on ice for a further 30 seconds.

2.7.1 Synthetic RTLF exposure

Once PM suspensions and controls (control positive, NIST and negative, M120) thawed at room temperature, both PM suspensions and controls were diluted to 55.56 g/ml using Chelex water with 5% methanol.

450µl of each PM suspension (in triplicate) were then pre-incubated at 37°C (Stuart Scientific Incubator S160) for 10 minutes prior to the addition of 50µl of the 2mM RTLF stock solution containing AA, GSH and UA. The PM samples and controls then incubated for an hour in the presence of an aliquot of synRTLF. PM samples and controls were incubated for 4 hours. They were then centrifuged (13,000 rpm) for 1 hour at 4^{o}C.

Below are descriptions of each protocol used for PM toxicity evaluation (Baker et al. 1990).

a. **Protocol 1:** Ascorbate-Urate (AA-UA) analysis using High Performance Liquid Chromatography (HPLC).

b. **Protocol 2:** Assay for glutathione by DTNB-enzyme re-cycling assay.

Protocol 1: Ascorbate-Urate (AA-UA) analysis using High Performance Liquid Chromatography (HPLC)

AA and UA concentrations were determined simultaneously using reverse phase HPLC with electrochemical detection (Iriyama et al., 1984). 20µl aliquots of each sample were injected for analysis using a Gilson model 231 auto-sampler onto a 15 x 4.6mm, 5µM SphereClone column, eluted with 0.2mM K_2HPO_4-H_3PO_4, containing 0.25mM octanesulphonic acid (pH 2.1) at a flow rate of 1.5ml/min. An EG&G amperometric electrochemical detector (Jones Chromatography, Hengoed, Wales) was used for detection, with E set at 400mV, a time constant of 5s, cathodic output and a sensitivity of 0.5-1µA. Sample concentrations were determined against a standard curve ascorbic acid (0-25µM) and uric acid (0-50µM) (both sigma) prepared in 5% MPA. Figure 2.13 shows an example of using the AA-UA standard curve to calculate unknown remaining AA-UA concentrations.

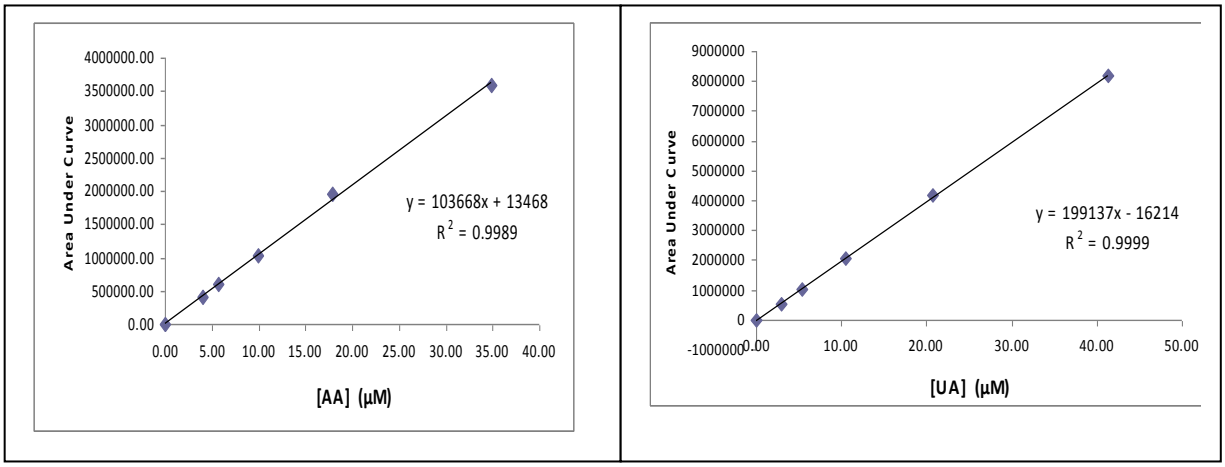


Figure 2.13: Typical standard curve for ascorbate [AA] and urate [UA] with r = 0.9989 and r = 0.9999, respectively.

Protocol 2: Assay for glutathione by DTNB-enzyme re-cycling assay

The determination of total glutathione (GSx) and glutathione disulphide (GSSG) in the samples and standards was based upon the DTNB-GSSG reductase re-cycling assay (adapted by Baker et al.1991). The assay is based on the non-enzymatic reaction of reduced glutathione (GSH) with 5,5'-dithiobis (2-nitrobenzoic acid)(DTNB) to produce GSSG and the coloured 5-thio-2-nitrobenzoic acid ion (TNB – Equation 2.1). TNB absorbs at 405nm and therefore its rate of formation can be monitored with time.

$$2GSH + DTNB \rightarrow GSSG + TNB \qquad \textbf{Equation 2.1}$$

In the presence of NADPH and the enzyme GSSG-reductase, GSSG can be enzymatically reduced back to GSH (Equation 2.2).

$$GSSG + NADPH + H^{+} \xrightarrow{GSSGreductase} 2GSH + NADP^{+} \qquad \textbf{Equation 2.2}$$

The regenerated GSH will then react with DTNB, again giving rise to enzyme re-cycling. To assay for GSx NADPH, DTNB and the sample are equilibrated, during which time all the GSH is oxidised to GSSG. The reaction is initiated by the addition of GSSG-reductase, with the formation of TNB monitored spectrophometrically; the absorbance being proportional to the GSx present. Measurement of the GSSG pool is achieved by conjugating the GSH in the sample to 2-vinyl pyridine such that the subsequent reduction of DNTB is entirely due to GSSG. Once the GSx and GSSG concentrations are known it is possible to express the concentration of GSH by subtracting 2xGSSG from the GSx concentration.

In order to measure GSSG, the GSH must be removed from the sample mixture. This was accomplished by conjugation of GSH to 2-vinyl pyridine. 130µl of each standard and sample were aliquoted into eppendorf tubes containing 5µl of 2-vinyl pyridine; the sample tubes were vortexed and then incubated for an hour at room temperature in a fume cupboard. After this incubation period 50µl from each tube was transferred in duplicate into a 96 well plate. 100µl of substrate was prepared and added as before, and the increase in A_{412}nm monitored

as outlined previously. GSH concentrations were calculated by subtracting the GSSG from the GSx concentration according to the following equation (Equation 2.3):

$$[GSH] = GSx - (2xGSSG) \qquad \textbf{Equation 2.3}$$

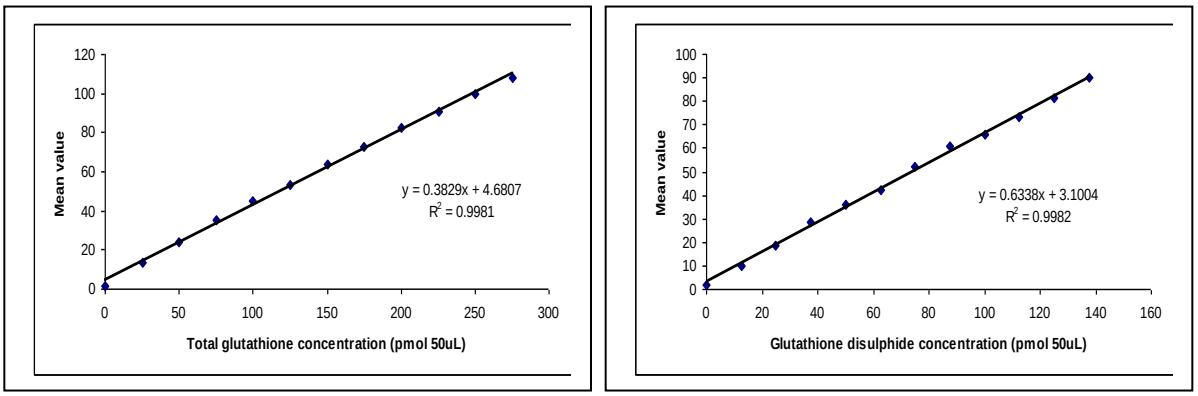


Figure 2.14: Typical standard curve for total glutathione [GSx] and glutathione disulphide [GSSG] with r=0.9981 and r=0.9962, respectively.

2.7.2 PM control samples &quality control

Accuracy and standardisation between PM samples and experiments in difference batches were achieved using positive, negative and PM filter blanks. PM control samples were run parallel with PM exposed MFG filters at equivalent concentrations. M120 containing black carbon particulate sample was used as negative control. A NIST worked as a positive control, containing the primary oil combustion process. Both of these PM control samples were extensively used in previous studies (Mudway et al. 2004, Duggan 2007, Godri et al. 2010). The PM filter blanks used in this study had similar characteristics as the PM exposed MFG filters. In order to ensure the efficiency of PM extraction from OSIRIS MFG filters, PM samples from a Tapered Element Oscillating Microbalance (TEOM) filter were used, which has been established in PM oxidative potential analyses in previous studies elsewhere (Mudway et al. 1999, Duggan 2007, Godri et al. 2010).

PM control samples, PM filter blanks and PM samples (OSIRIS MFG filters and TEOM filters) were taken through the extraction process and the resulting supernatant analysed for oxidative potential activity as demonstrated in Figure 2.15.

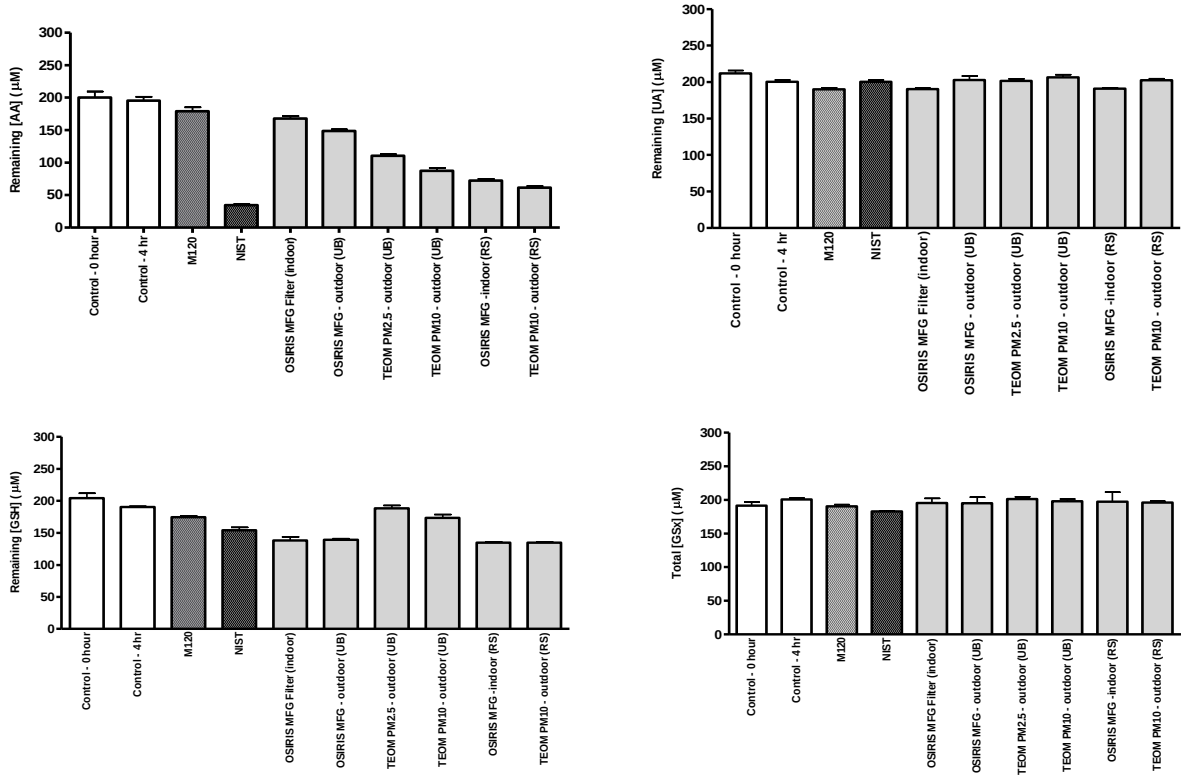


Figure 2.15: Comparison of mean ± standard deviation between blank controls (0 and 4 hours of incubation at 37^{o}C) with positive controls (M120), negative control (NIST) and exposed PM filters *.

*Notes: * Exposure time periods were different according to filter types: OSIRIS MFG indoor-outdoor – 1 week exposure; TEOM UB outdoor – 2-3 months exposure; and TEOM RS outdoor – 1week exposure. UB = urban background site & RS = roadside site.*

2.8 PM oxidative potential (OP) metrics

PM OP data output was presented in two different unit metrics: per unit mass (OP $^{AA\ or\ GSH}$ μg^{-1}) and per unit volume (OP $^{AA\ or\ GSH}$ m^{-3}). PM OP unit metrics were derived from the following set of calculations. The percentage loss of AA or GSH was determined by the remaining AA or GSH concentration in the synthetic RTLF in PM samples relative to particle free control after four hours of incubation (as stated in Calculation 2.1). PM OP metrics per unit mass, OP $^{AA\ or\ GSH}$ μg^{-1}, were achieved by normalizing the percentage of antioxidant depletion obtained from Calculation 1 using 150µg ml^{-1} as the final PM concentration used in the RTLF incubation (Calculation 2.2).

Multiplication of PM OP per unit mass with PM concentration, depending on whether PM filters were exposed to either ambient (outdoor) or indoor PM concentration, produced PM OP metric per unit volume, OP $^{AA\ or\ GSH}$ m^{-3} (Calculation 2.3).

Calculations 2.1 – 2.3 are presented for individual PM source of environment exposure (outdoor or indoor environment). PM OP metrics calculations are as follows:

$$\%\,\text{Loss of AA @ GSH} = \frac{\text{PM sample AA @ GSH } (\mu\text{M})}{\text{PM control 4-hour blank } (\mu\text{M})} \times 100 \qquad \textbf{Calculation 2.1}$$

$$\frac{OP^{AA@GSH}}{\mu g} = \frac{\%\,\text{Loss of AA @ GSH}}{50\,(\mu g\ mL^{-1})} \qquad \textbf{Calculation 2.2}$$

$$\frac{OP^{AA@GSH}}{m^3} = \frac{OP^{AA@GSH} \big/ \mu g}{PM\ Concentration\,(\mu g\ m^{-3})^*} \qquad \textbf{Calculation 2.3}$$

*Notes: * depending on PM source of exposure; either outdoor or indoor PM concentration*.

2.9 Monitoring data plot & statistical analysis

Analysis of continuous indoor-outdoor pollutant data sets was processed and analysed using Monnet 2.0 and converted into data in Microsoft Excel using SQL Management Studio 2007. Statistical software called 'open-air' package R-software was used to obtain diurnal plotting variables gathered from the long term monitoring database (Carslaw&Ropkins – website address: *www.openair-project.org*. R-language was applied to Tinn-R tools to produce graphic outputs, which were saved as metafile images.

In terms of the relationships between pollutant variables, correlation and regression analysis techniques were calculated to estimate the mean value of a dependent variable contribution for any given value of the independent variables. In addition, the mean distributions for each variable parameter were demonstrated as a box plot analysis. Most data were plotted and displayed graphically using GraphPad Prism 5 and SigmaPlot 12.0.

Indoor and outdoor variable parameters were summarised using descriptive statistics. Statistical analyses were carried out using SPSS software, version 18 for Windows (Statistical Package for the Social Sciences, Chicago, IL, US).

Chapter III

Case study 1 –I/O transferof pollutants in a naturally ventilated suburban school building

3.1 Introduction

Recently, much attention has been focusedon monitoring air quality in environments such as homes (Taneja et al. 2008), vehicles (Pang et al. 2007) and classrooms(Branis et al. 2005, Branis & Safranek 2011, Branis et al. 2011). A wealth of evidence has demonstrated the relationship between SBS syndrome and poor IAQ, particularly amongst fragile groups including children (e.g. Nazaroff 2005, Biette et al. 2008, Breysse et al. 2010). In the UK, children spend 90% of their time inschool classrooms, and their condition is very important for student health and academic performance (Carslaw et al. 2009). Hence, indoor air quality in the school environment plays a major role in determining a better indoor environment for school children(Daisey et al. 2003, Crump et al. 2005).

Generally, indoor pollutant concentrationsare derived from two sources: indoor and outdoor. However, the correlation between both sources variesaccording to the influence factors, including building characteristics (ventilation type and opening doors/windows),as well as aerodynamic diameter particles emitted – that is, particle suspension (Long et al. 2000, Alshitawi & Awbi 2011).

Thus, the main exercise in this chapter is to characterise both pollutant concentrations derived from outside and inside the building. Long term monitoring of gaseous pollutants and airborne PM is discussed, considering the influences of meteorological conditions and building use.

3.1.1 Site sampling and description

The description of site selection, data monitoring and analysers involved in this study were discussed in Chapter II. Briefly, the Environmental Curricular Centre is situated in a London suburb located 5km west of Eltham city centre, London Borough of Greenwich. Owing to the garden and golf course directly opposite, this building is minimally exposed to external pollution. The indoor sampling site was installed in the frequently used classroom, which was predominately used for environment-related art activities such as painting, drawing and paper-making by children aged between 8–12 years. Therefore, a large number of bottles, plates for garden soil and liquids were present in many locations within the classroom. One of the classrooms in this study has one window without any ventilators, as well as two access doors to the other classroom, mainly used as a library.

In addition, a building diary was recorded throughout the study campaign. School activities, a visitors' diary, and teaching materials used in the classroom were recorded by the school administrator in order to keep track of the classroom's condition. Average student attendance was quantified using a personal-hour indicator. A manual log book and teaching diary were used to clarify these school activities. The building diary data was collected during fortnightly visits to this site. However, ventilation conditions controlled by the opening of doors/windows were not recorded in this study due to the difficulty of data collection. In a previous study, tracer gas measurements (i.e. sulphur hexafluoride [SF_6] and carbon dioxide [CO_2]) were used to calculate the air exchange rate (AER) in different types of scenarios, such as the frequency of opening doors/windows (Alshitawi et al. 2009). The determination of AER was identified by the decay measurement rate with an appropriate instrument (Guo et al. 2008). Due to the difficulty of recording opening doors/windows on a long term basis, the AER, which is one of the cofounders in this study, was indicated by the assumption that doors and windows are opened more frequently during summer. In addition, by using a cleaning routine diary, cleaning products used and building maintenance proven to influence indoor emission was also categorised as a confounder.

Pollutant parameters measured in this study were gaseous pollutant species (NO_X, NO_2 and O_3) and airborne particulate matter (PM_{10}& $PM_{2.5}$). Both of the indoor and outdoor parameters were monitored parallel to each other.

3.1.2 Research aims and objectives

This study aims to assess and to establish the relationship between indoor-outdoor pollutants concentrations via spatial and temporal descriptive analysisbased on the long term monitoring dataset which was established in this study. Specifically, the main objectives of this chapter are as follows:

a. The differences of indoor-outdoor pollutants concentration according to the long term diurnal variation profiles.
b. The differences of indoor-outdoor pollutants concentration according to meteorological condition (wind speed and wind direction).
c. The differences of indoor-outdoor pollutants concentration according to building use under different time measurement scenarios (occupied, partially occupied, weekend and public holiday).
d. The differences of indoor-outdoor pollutants concentration according to the seasonal variation.

3.2 Long term indoor-outdoor monitoring database

Methods of data capture, ratification and data management for this study are described in Chapter II, section 2.4. Monitoring at this site ran from August 2008 until June 2011. However, due to complications with the instrument and permission agreements prior to installation at this site, airborne particulate monitoring was delayed and only ran from March 2010 until March 2011. As shown in Table 3.1, indoor-outdoor gaseous pollutant monitoring achieved greater than 90% valid data. However, due to instrument failure in the beginning of the monitoring period, indoor and outdoor PM data capture rates were 71% ± 2.

Table 3.1: Monitoring data summary statistics from naturally ventilated school building.

Pollutant species	Sampling inlets	Mean ($\mu g\ m^{-3}$)	95 percentile ($\mu g\ m^{-3}$)	Capture Rate (%)
NO_X	Indoor	25.5	55.9	90.5
	Outdoor	20.0	67.8	91.6
NO_2	Indoor	8.4	15.7	90.5
	Outdoor	13.2	34.0	91.6
O_3	Indoor	1.4	5.5	96.9
	Outdoor	13.2	39.5	97.4
PM_{10}	Indoor	3.9	11.7	74.2
	Outdoor	14	30.6	72.7
$PM_{2.5}$	Indoor	21.3	89.0	72.7
	Outdoor	6.1	14.9	70.4

Notes: Monitoring data on gaseous pollutants (NO_X, NO_2 and O_3) were captured from August 2008–June 2011, whereas for particulate matter (PM_{10} and $PM_{2.5}$) data were captured from March 2010–March 2011.

Figure 3.1 and 3.2 illustrated the long-term time series continuous monitoring for pollutant parameters measured at this site. Time series measurement for gaseous pollutant for NO_X and NO_2 was inconsistent throughout the monitoring campaign, plus high peak concentration measured at certain point represented as little 'spike'. Interestingly, O_3 indoor concentration showed a similar pattern constantly with higher concentration in the middle of the year, particularly during summer time. Further, PM_{10} and $PM_{2.5}$ indoor showed a different pattern when compared to outdoor concentration. The patterns of indoor PM concentrations were illustrated with high peak concentration at certain time of monitoring periods. However, outdoor PM concentration was constantly measuredthroughout the monitoring campaign.

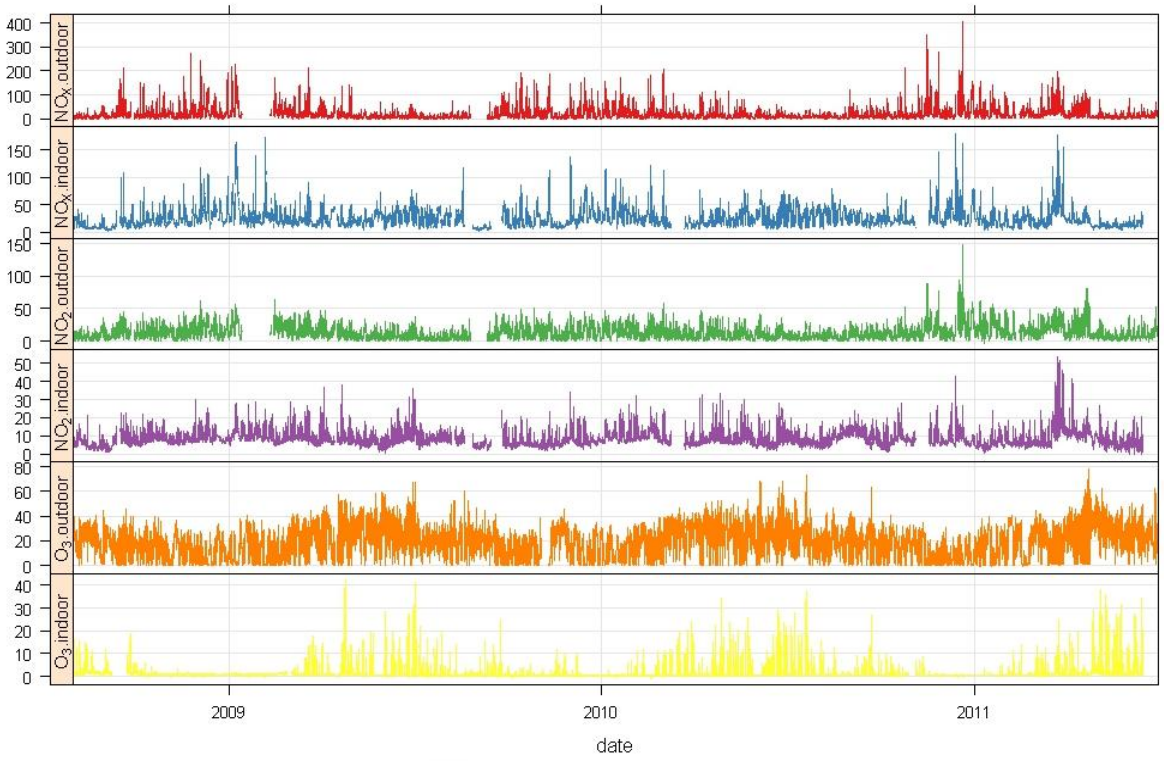


Figure 3.1: Time series plot for indoor-outdoor gaseous pollutant species monitored from August 2008-June 2011.

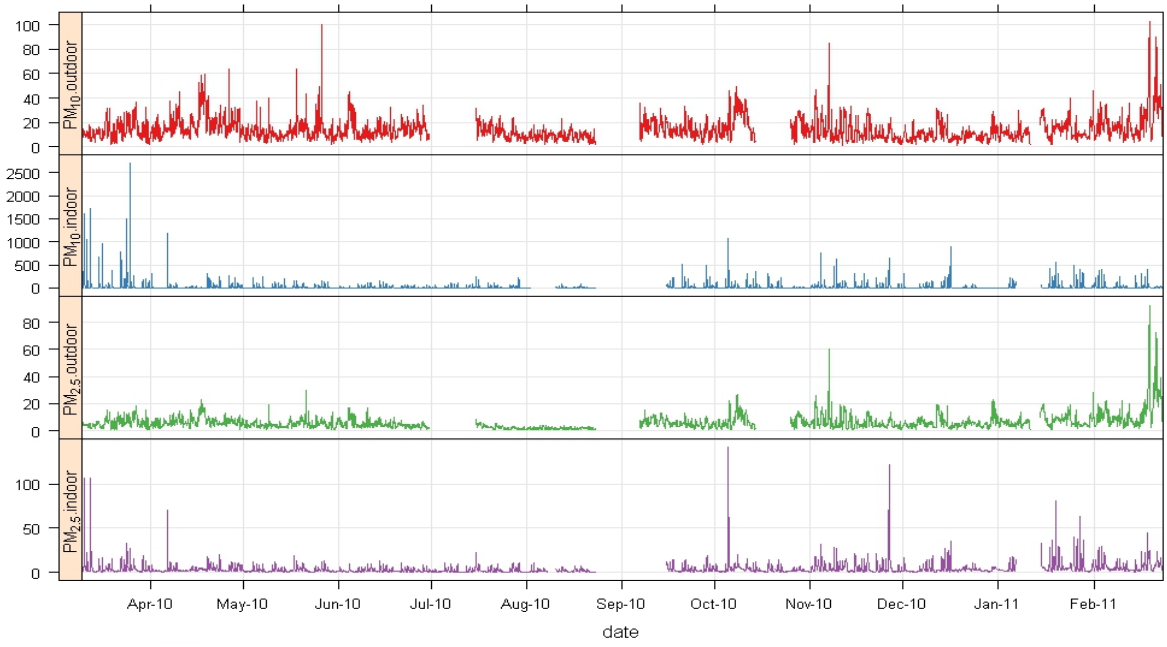


Figure 3.2: Time series plot for indoor-outdoor particulate matters monitored from March 2010-March 2011.

Notes:*Each of the pollutant parameters in both of figures above were in different scales in caption.*

3.2.1 Diurnal variation profile

3.2.1.1 Indoor-outdoor gaseous pollutants (NO_X, NO_2 and O_3)

Figure 3.3 shows a diurnal variation profile for NO_X, NO_2 and O_3. Three different averaging periods are illustrated in this figure; hourly variation, daily variation and monthly variation. The data processing and output analyses were produced using the open-air package in R statistical software.

Hourly variation profile (NO_X): The outdoor NO_X concentration was observed to have a different pattern when compared to the indoor NO_X concentration. High concentrations of outdoor NO_X were recorded throughout the 24 hour monitoring. In detail, at the beginning of the day (0000-0400 hours), outdoor NO_X was at its lowest concentration (averaging 16 µg m^{-3}), which contrasted with indoor NO_X, which was constant at its highest concentration. The indoor NO_X constant value was about 28 µg m^{-3}. Outdoor NO_X concentration then rapidly increased to similar concentrations to indoor NO_X,between 0400 and 0900. The concentration of outdoor NO_X then dropped until 1200 hours, and gradually increased up to 24 µg m^{-3}at 1800 hours, whereas indoor NO_X concentration remained at a constant concentration even when it was observed dipped in the afternoon. From 1800-2300 hours, outdoor NO_X continued to decrease, reaching its minimal concentration, mean 16 µg m^{-3}, while indoor NO_X had a constant concentration at 26 µg m^{-3}.

Hourly variation profile (NO_2): The indoor NO_2 concentration profile was lower than the outdoor NO_2 concentration profile. Initially, between 0000-0400 hours, indoor and outdoor NO_2 concentrations were their lowest, averaging 7 µg m^{-3} and 10 µg m^{-3}, respectively. Between 0500-0900 hours, outdoor NO_2 concentration rapidly increased to almost 16 µg m^{-3}. It then decreased gradually to 10 µg m^{-3}, followed by an increment of indoor NO_2 at a similar concentration. Further, between0900-1800 hours, indoor and outdoor NO_2 concentrations remained at the same concentration, . Between 1800-2300 hours, outdoor NO_2concentrations were higher than indoor NO_2 concentration; indoor NO_2 decreased to its minimum concentration.

Hourly variation profile (O_3): The indoor O_3 concentration profile was at its lowest while the classroom was unoccupied (0000-0900 hours), averaging between 2-4 µg m^{-3}. However, indoor O_3 concentration increased while the classroom was occupied classroom (0900-1800 hours) with mean 4 µg m^{-3}, whereas outdoor O_3 concentration was recorded as higher than indoors and reached its maximum concentration at 28 µg m^{-3}, particularly during mid-day.

Weekly variation profile: From Monday to Friday, daily mean outdoor NO_2 and O_3 concentrations were higher than indoors, recorded as 14 µg m^{-3} and 20 µg m^{-3} outdoors, and 9 µg m^{-3} and 3 µg m^{-3} indoors, respectively. However, indoor NO_X was higher than outdoor NO_X, which was mainly dominated by the proportion of NO, mean 25 µg m^{-3}. The domination of indoor NO concentration continued to increase at the weekend. Further, for indoor NO_2 and O_3 concentrations, both of these pollutants recorded their minimal concentrations.

Monthly observation profile: In 3 years of observation, from 2008-2010, outdoor NO_2 and O_3 were always higher than indoors. Indoor NO_X, was higher than outdoors particularly during summer time.

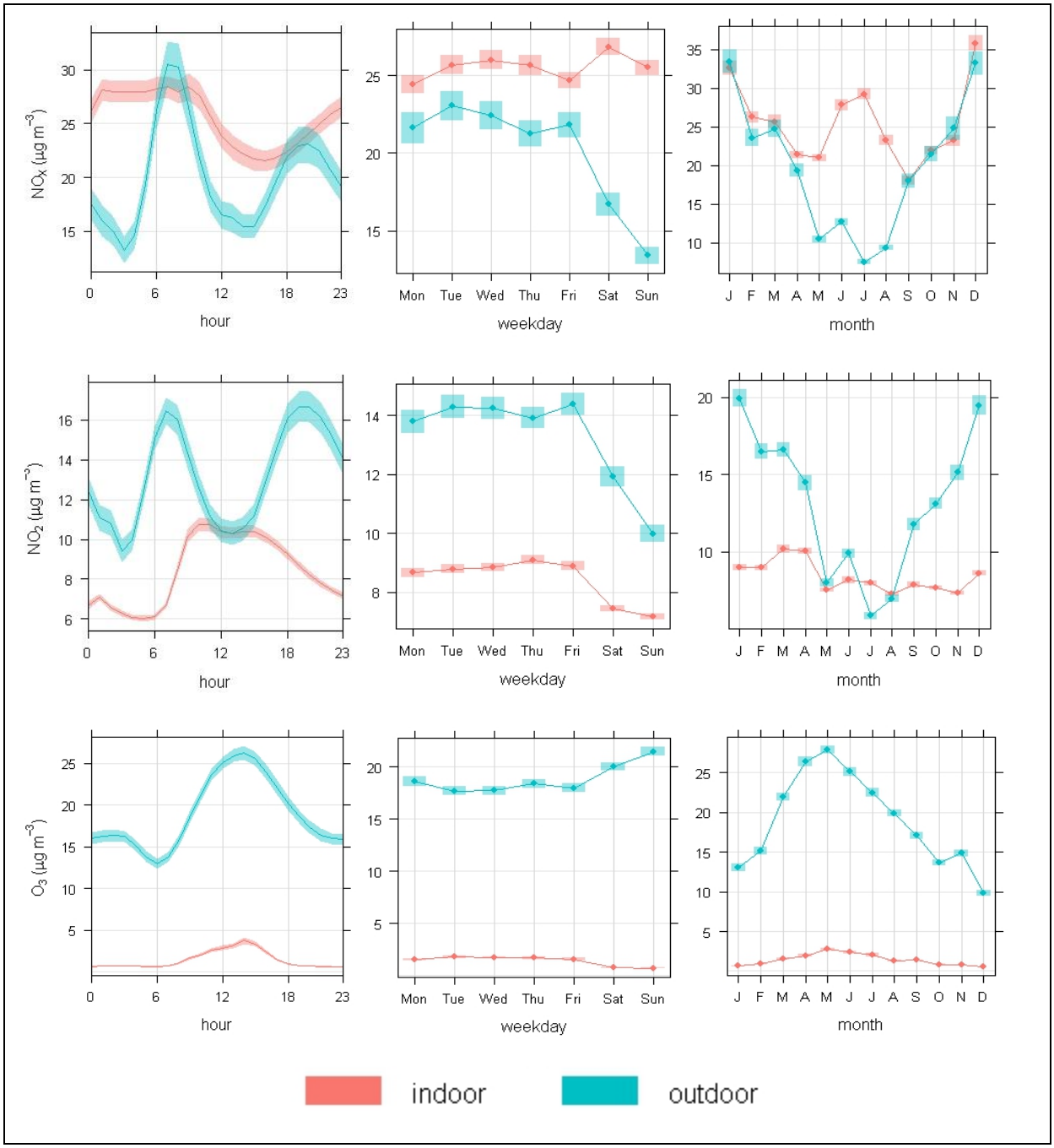


Figure 3.3: Diurnal variation profile (hourly-weekly-monthly) for indoor-outdoor NO_X, NO_2 and O_3, at naturally ventilated school building.

Generally, diurnal variation profile in figure above showed that the hourly variation profiles for NO_X and NO_2 concentrations were recorded with rapid elevation during rush hour. Although this building was considered to be away from the direct primary source of vehicle combustion, the usage of the parking lot located in front of the school building may indicate such an increment. The parking lot space was used not only by staff, but also by other vehicles such as the school bus and other vehicles for transporting garden materials to the back of the building. Further, the opening of doors and windows during rush hour (from 0800-0900 hours) may indicate the penetration from outdoor vehicular combustion sources and contribute to the increment of indoor NO_X and NO_2 inside the classroom. This phenomenon also affected indoor O_3, which indicated penetration from outdoor O_3 when the building was occupied.

However, the increase of indoor NO_X concentration during unoccupied periods is still questionable. The indoor NO_X concentration was observed as higher than outdoors, and continued to increase, particularly during the night. With the absence of penetration issues while the building was unoccupied, this concentration may correlate to the existence of indoor sources inside the classroom.

Furthermore, weekly variation profiles may indicate similar findings observed in hourly variation profiles. The existence of indoor NO sources may indicate the increment of indoor NO_X at the weekend. However, this finding is still subjective. Indoor NO sources inside the classroom could be from a variety of emission factors and building conditions such as building materials, furniture and the heating system (boiler).

In addition, from monthly observation, higher NO_2 and O_3 concentrations occurring indoors are possibly explained by the penetration issues resulting from windows and doors being frequently opened, particularly during summer time.

3.2.1.2 Indoor-outdoor airborne PM airborne (PM_{10} and $PM_{2.5}$)

Indoor-outdoor PM airborne monitoring at this site began in March 2010 and lasted until March 2011. Two PM size fractions were logged, PM_{10} and $PM_{2.5}$. These parameters were recorded parallel to the indoor-outdoor gaseous pollutant species; the results are shown in Figure 3.4.

Hourly variation profile: Different patterns of concentrations were clearly observed. Outdoor PM_{10} and $PM_{2.5}$ were recorded almost at constant concentrations throughout the 24 hour period. However, indoor concentrations for both PM size fractions were recorded with high peak concentration during occupied periods. In detail, between 0000-0600 hours, indoor PM was recorded at its minimal concentrations, averaging 8 µg $m^{-3}$and 2 µg m^{-3} for PM_{10} and $PM_{2.5}$, respectively. However, rapid increases of indoor PM concentration were recorded when the building was opened during rush hour (0600-0900 hours), with means of 70 µg $m^{-3}$and 7 µg m^{-3} for PM_{10} and $PM_{2.5}$, respectively. Furthermore, these concentrations dropped gradually between 0900-1800 hours, to about 40 and 6 µg m^{-3}, respectively. It continued to drop and remained at minimal concentration.

In contrast, outdoor PM concentration (PM_{10} and $PM_{2.5}$) remained constant throughout the day, with means of 18 µg m^{-3} and 6 µg m^{-3}, respectively.

Weekly variation profile: Indoor PM_{10} concentration was observed to be higher than outdoors, but not for indoor $PM_{2.5}$. It was recorded as lower during weekdays. However, both of these indoor concentrations were recorded at their lowest concentrations at the weekend. In contrast, outdoor concentration remained at the same concentration throughout the week.

Monthly variation profile: One year of monitoring shows that indoor PM concentrations had similar patterns to those outdoors. However, indoor PM_{10} concentration was always higher than outdoor concentration throughout the year.

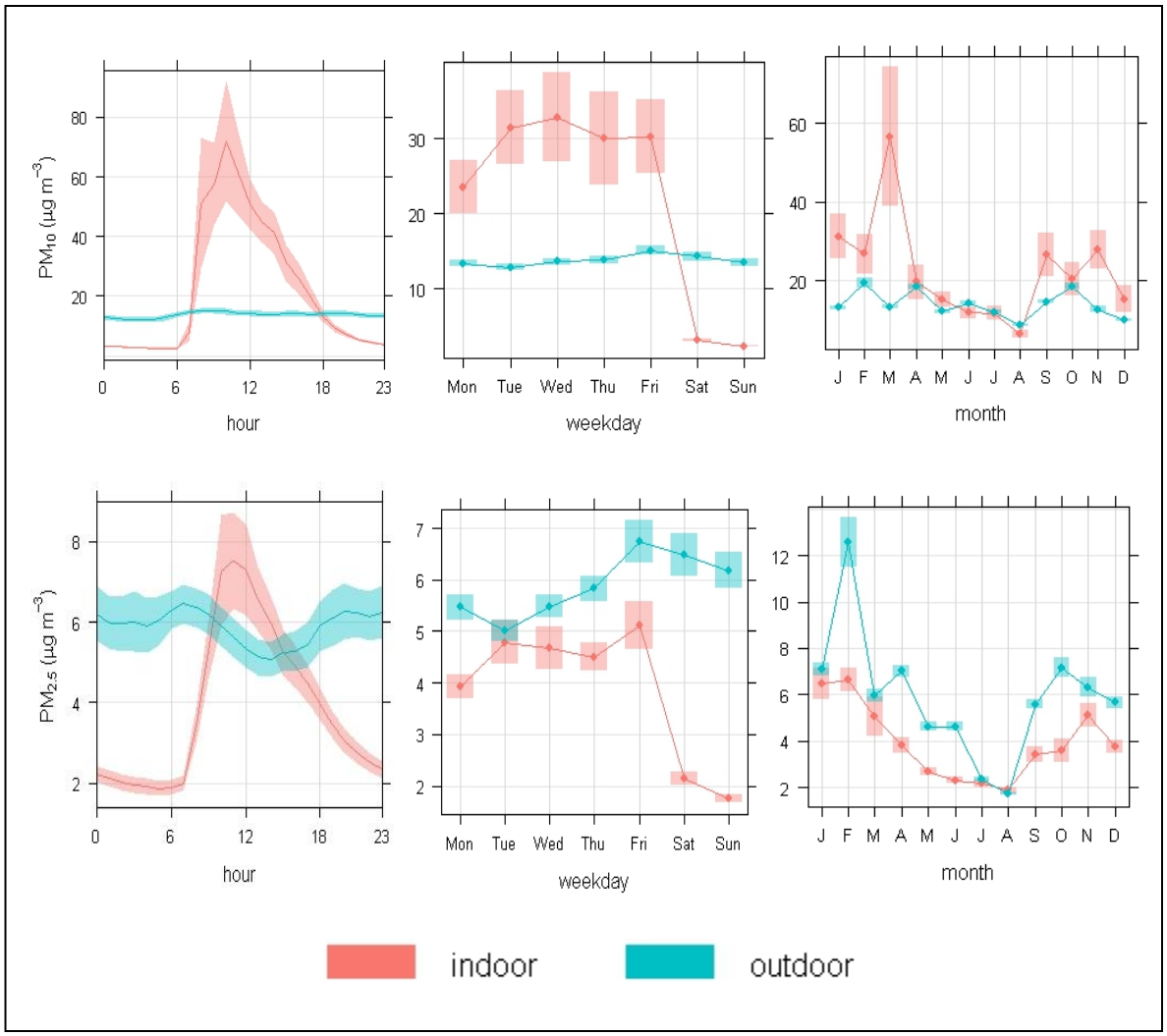


Figure 3.4: Diurnal variation profile (hourly-weekly-monthly) for indoor-outdoor PM_{10}& $PM_{2.5,}$ naturally ventilated school building.

Generally, indoor PM concentrations of PM_{10} and $PM_{2.5}$ were observed to be higher, particularly at the beginning and at the end of class activity. These concentration patterns may thus possibly explain the PM suspension via building occupancy. Indeed, the highest concentration was normally recorded at 1100 hours, when the classroom was packed with children and class activity. Building diary data show that the paper-making and environmental-related activities inside the classroom, the latter of which used garden soil, correlate with the local peak of indoor PM in this building (see data in Appendix A). Furthermore, a daily mean indoor PM observed to be higher than outdoors during

weekdays was driven by a similar situation. These concentrations dropped to their minimums, whereas the outdoor PM concentration remained the same. In addition, monthly observation shows these concentrations reached their maximum concentration during the winter, when the window was shut most of the time. Lack of ventilation and particles trapped inside the classroom may have led to such concentration patterns. In contrast, the indoor PM concentration dropped during summer time, when the doors and windows are frequently opened. However, these concentrations levelled out during this period, which may indicate the association between indoor and outdoor sources.

3.3 Meteorological conditions

The air tightness of a building can increase protection from outdoor sources. However, the relationship between indoor and outdoor pollutants varies inside naturally ventilated buildings, which depend on parameters such as air exchange rates, window-opening, use of exhaust fans as well as meteorological conditions (Wallace et al. 2002). Indeed, the dispersion of pollutants in the atmosphere and the pollutants transferred into the building were influenced by wind speed and direction (Murray & Burmaster 1995, Emmerich & Nabinger 2001). In this section, polar frequency plots were analysed to describe the pollutant concentration distributions inside and outside the study building by inserting wind speed and direction measurements.

In general, a polar frequency plot is interpreted by the number of hours coded into a colour scale. The scale itself is non-linear to show overall distribution; dashed circular grey lines show the wind speed scale, as shown in Figure 3.5. As mentioned in Chapter II, section 2.1, meteorological data from Bexley 2 was used for this study site to represent general atmospheric conditions deriving from a homogenous local source at both study sites.

Indoor-outdoor gaseous pollutants and particulate matter

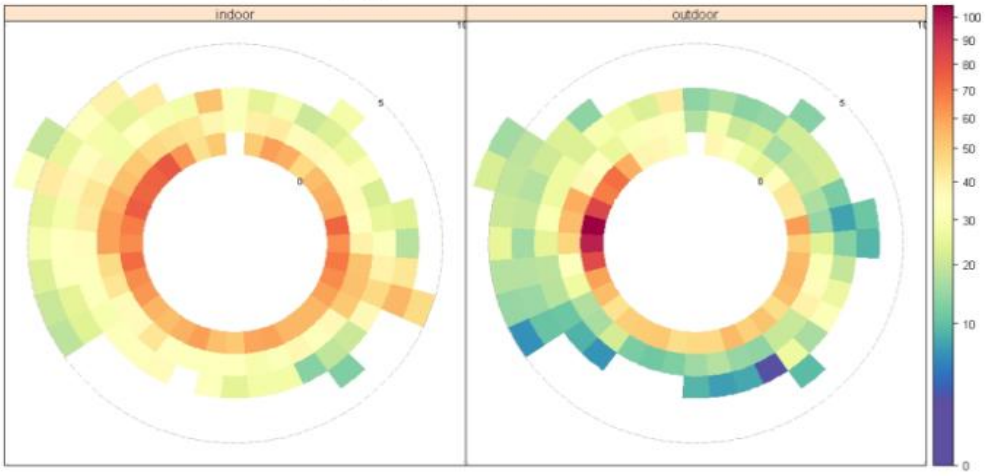
Generally, the colour scale contrast between indoor-outdoor gaseous pollutants and particulate matter shows a different pattern of distribution. The proportional values of outdoor NO_X concentration were distributed between 30-100 µg m^{-3}, whereas indoor NO_X concentration was in the range of 20-80 µg m^{-3}. Indoor and outdoor

O_3concentrations were distributed between 20-80 µg $m^{-3}$and 0-20 µg m^{-3}, respectively. Further, the hourly mean of outdoor NO_X concentration was distributed from an east to westerly direction at speeds of less than 5 m s^{-1}. However, indoor pollutant concentrations were spread evenly inside the building. This finding also shows a similar pattern to O_3 concentration. The results show that outdoor O_3 concentration was higher than indoor concentration but there is no clear evidence to show the influence of wind speed and direction causing the transportation of outdoor pollutants indoors.

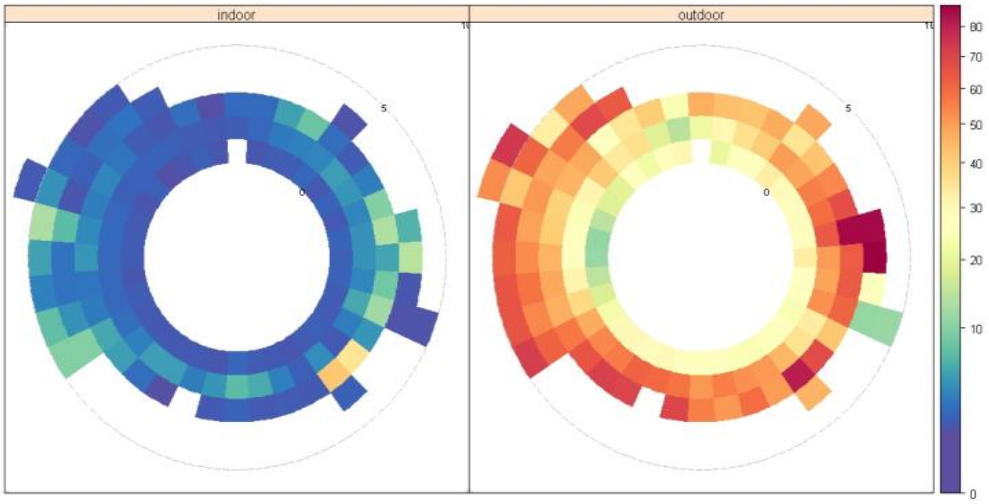
The colour scale contrast for particulates in Figure 3.5 shows that outdoor PM_{10} and $PM_{2.5}$ concentrations were distributed between south-easterly to north-westerly directions with speed less than 2 m s^{-1}. However, the majority of indoor PM_{10} and $PM_{2.5}$concentration was fairly distributed. In addition, the colour scale shows a higher concentration of indoor PM_{10} and $PM_{2.5}$, averaging 50-110 µg $m^{-3}$and 6-15 µg m^{-3}, respectively.

This finding also suggests that there is no clear evidence to show the effects of meteorological conditions on outdoor PM transportation inside the classroom. However, the judgement of this finding is still subjective for definite conclusion, since most of the meteorological data at this site was relied on BX 2 – remote site, which was noticed as a limitation for this study. These results could be differed by the atmospheric condition and also derived by the local pollutant sources.

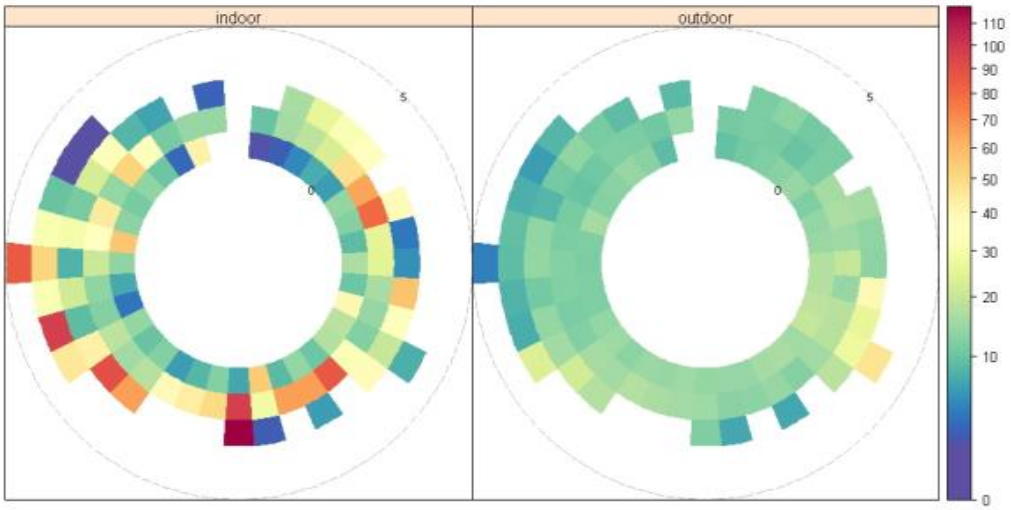
NO_X (in ppb) at natural ventilated school building



O_3 (in ppb) at natural ventilated school building



PM_{10} at natural ventilated school



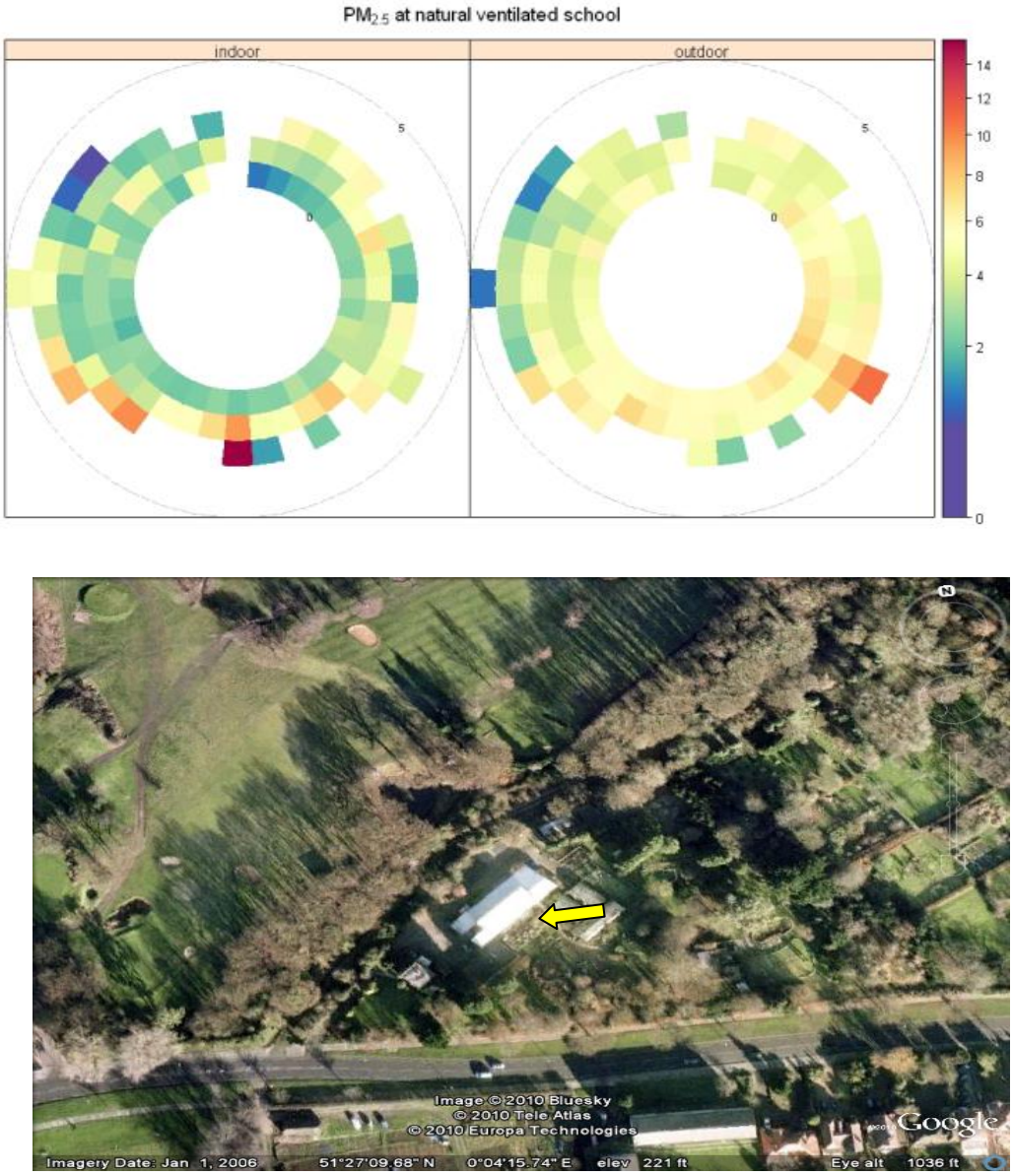


Figure 3.5: Polar frequency plot between indoor-outdoor gaseous pollutants (NO_X& O_3) and particulate matter (PM_{10}& $PM_{2.5}$) concentrations in naturally ventilated school building.
Notes:Colour contrast represents gaseous pollutant concentrations in µg m^{-3}. Yellow pointer shows the window position of the classroom.

3.4 Building occupancy: Indoor-outdoor data monitoring comparison

In order to ascertain the influence of the presence and absence of occupiers (including teachers and students) on indoor-outdoor pollutant concentrations in the school building, the data obtained during the course of the 1-year monitoring campaign is divided into 4 measurement time periods:

a. Occupied (0900-1630 hours; classroom has been used by students and teachers).
b. Partially occupied (0900-1630 hours; teacher-on-duty and classroom has been used intermittently).
c. Weekend.
d. Public and school holiday (site closure; term break according to the school diary).

Ratio analysis

In general, I/O ratio determination indicates the strength of indoor sources, which could highly vary depending on the indoor activities and outdoor concentration levels. Figures 3.6 and 3.7 show the ratio mean plotted with standard deviation (SD) to represent a spatial distribution with the respective values of I/O ratio according to 4-measurement time periods.

Overall, I/O ratio NO_X was observed to be higher than 1.0 except for public holidays. Further, the NO ratio was dominated by indoor NO sources, indicating that the I/O NO ratio was higher than 1.0 at most of the time measurement periods (as shown in Figure 3.6). The highest I/O NO ratio was recorded during unoccupied periods, particularly at the weekend. This finding indicates a similar conclusion as that observed in the diurnal variation profile, with increments of indoor NO concentration at night time and the weekend. These I/O ratio patterns may thus prove that a possible indoor NO source may exist inside the classroom during unoccupied periods. However, for NO_2 and O_3, there was no indoor issue for either of these pollutant species.

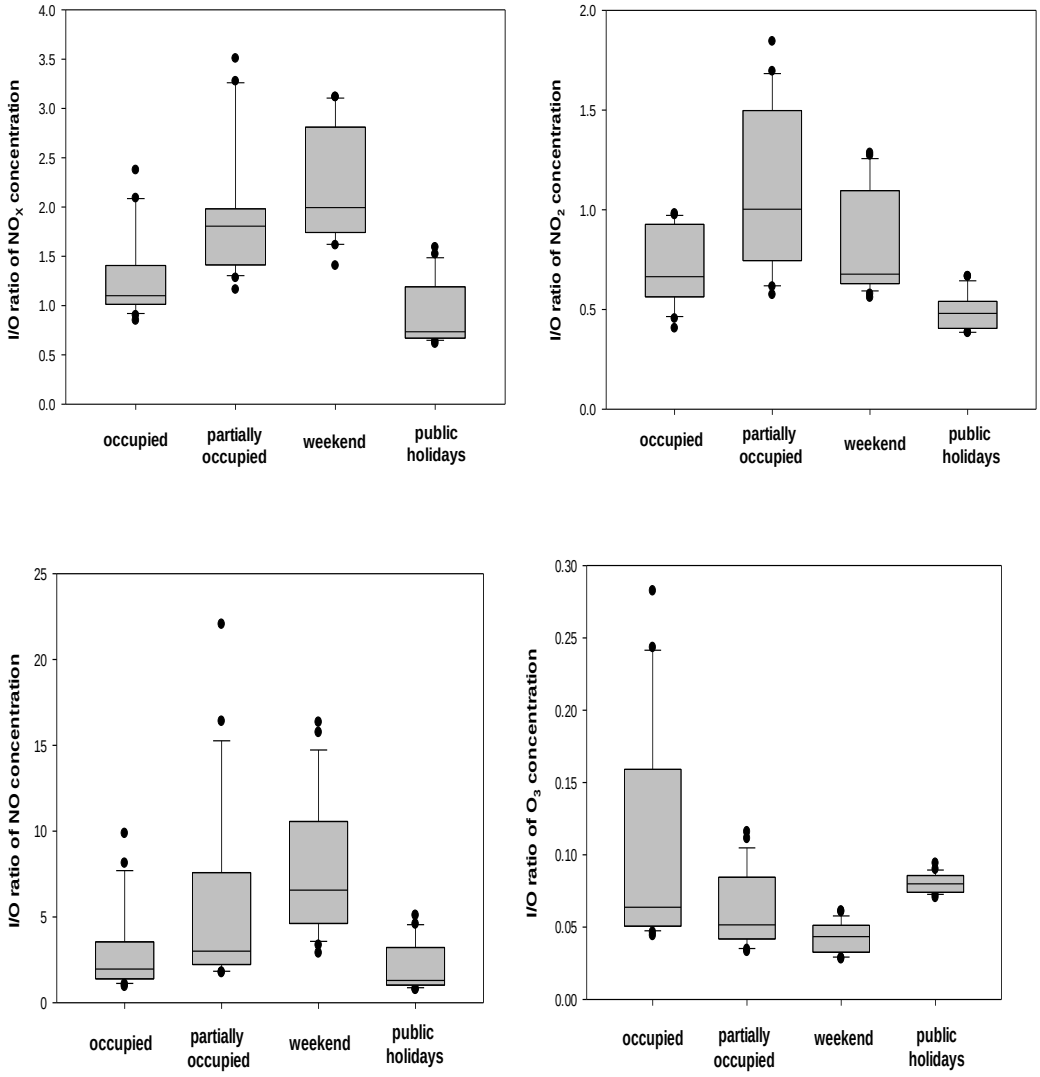


Figure 3.6: I/O ratio for gaseous pollutant species in different time measurement periods, naturally ventilated school building.

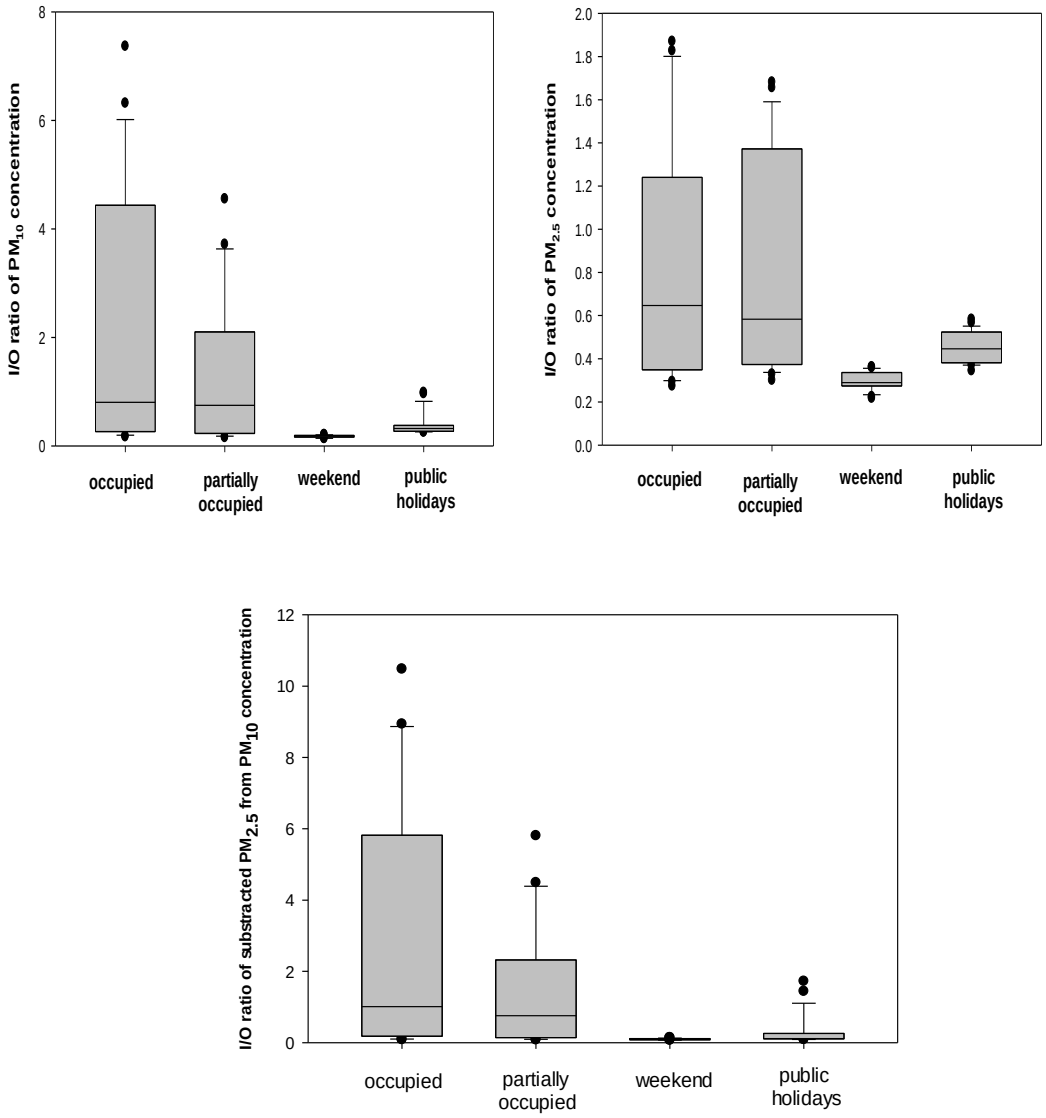


Figure 3.7: I/O ratio for airborne particulate matter in different time measurement periods, naturally ventilated school building.

Furthermore, I/O ratio for particulate matter for both selected sizes was observed to be higher during occupied periods. Figure 3.7 shows that the highest I/O ratio PM_{10} (more than 1.0) was recorded during occupied and partially occupied periods. The same finding was also observed for the subtracted $PM_{2.5}$ from PM_{10} (to investigate the coarse PM components). These finding shows that the higher ratio (more than 1.0) could explain the role of occupancy pattern via certain type of classroom activity could be a major influence factor contributing to a local source of indoor PM. The influence of building diary activity (classroom activity) on the diurnal variation profile will be discussed further in the next section.

Correlation analysis

Correlation of indoor and outdoor concentrations can imply a source relationship between indoor-outdoor environments. Therefore, the indoor and outdoor correlations for gaseous pollutants and airborne PM in different time measurement periods were analysed to determine the dependency of indoor pollutants on their corresponding outdoor pollutant concentration.

Generally, in Table 3.2, O_3 and PM_{10} show a strong correlation between indoor-outdoor concentrations, specifically during occupied periods, with r-values ranging between 0.82-0.86 and 0.75-0.77, respectively. The agreement between indoor-outdoor concentrations shows an R^2 of 0.74; this determines that the indoor O_3 can explain about 74% of the variation of outdoor O_3 concentration. Indeed, the variation of indoor PM_{10} was about 59% from the outdoor source. However, the variations for particulate concentration were varied due to building occupancy factors. These findings revealed the penetration of outdoor pollutants into the classroom.

In contrast, other parameters showed poor correlation in all time measurement periods. This finding shows a weak contribution of outdoor sources into the classroom. It may prove a previous finding that the independent indoor source exists inside the building. In addition to the above correlation, indoor-outdoor NO correlation showed significant positive and negative correlation at the weekend and public/school holidays, respectively. These findings may possibly explain the increment of indoor NO concentration at night time and the weekend.

Table 3.2: Correlation coefficients between indoor and outdoor pollutant species, naturally ventilated school building.

Pollutant species	**Occupied**	**Partially occupied**	**Weekend**	**Public / School holiday**
	Correlation coefficient, r-values			
NO_Xin/NO_X out	0.108	0.490 *	0.518 **	-0.319
NO_2 in/ NO_2 out	-0.007	-0.405 *	-0.605 **	0.546 **
NO in/ NO out	-0.016	0.350	0.771 **	-0.628 **
O_3 in/ O_3 out	0.858 **	0.816 **	0.452 *	0.633 **
PM_{10} in/ PM_{10} out	0.749 **	0.772 **	0.285	0.269
$PM_{2.5}$ in/ $PM_{2.5}$ out	-0.205	-0.390	0.595 **	0.148

*Notes: Occupied (0900-1630, classroom has been used by students and teachers);Partially occupied (0900-1630, teacher-on-duty and classroom has been used intermittently); Weekend, Public/school holiday (site closure, term break according to school diary). Significant p-value (less than 0.05 **).*

3.5 Building occupancy: Indoor-outdoor pollutant diurnal variation profile

Figures3.8and3.9illustrate the time series (average 15 minutes) of indoor and outdoor gaseous pollutant species and airborne particulate matter under different time measurement scenarios. The classroom data analysed for this investigation was obtained from the 24-hour monitoring of each scenario, and was compared to recorded daily diary activity.

Gaseous pollutant species

Indoor gaseous pollutant species were not influenced by occupant activity and behaviour.Interestingly, indoor NO_X concentration was observed to be higher during unoccupied periods (early morning) between 0000-0700 hours. The level of indoor NO_X concentration decreased to its minimal concentration when the school day started with teaching slots and curricular activity. The majority of the indoor NO_X was attributed to the NO source.

In contrast, indoor O_3 concentration gradually increased during this time,whereas indoor NO_2 was lower, with a mean of 8 µg m^{-3} during occupied periods.However, outdoor gaseous pollutant concentration changed very little throughout the 24-hour monitoring campaign, except for a rapid peak increase of outdoor NO_X during the rush hour of 0800-0900 hours. The indoor concentration for NO_X (mainly for indoor NO) was elevated again after school ended and the doors and windows were closed during the night. However, indoor O_3 was gradually reduced to its minimum concentration.Thus, indoor concentration of gaseous pollutant species could be influenced by building occupancy, especially for O_3. Penetration issues may possibly explain the increment in concentration during occupied periods when doors and windows were opened.

The high proportion of indoor NO sources during unoccupied periods seemed to dominate throughout the monitoring campaign, especially at night time and the weekend. This can be further examined to investigate any indoor NO sources inside the classroom.

Figure 3.8: Indoor and outdoor PM variation profiles according to 4 time measurement periods (occupied, partially occupied, weekend and school/public holiday).

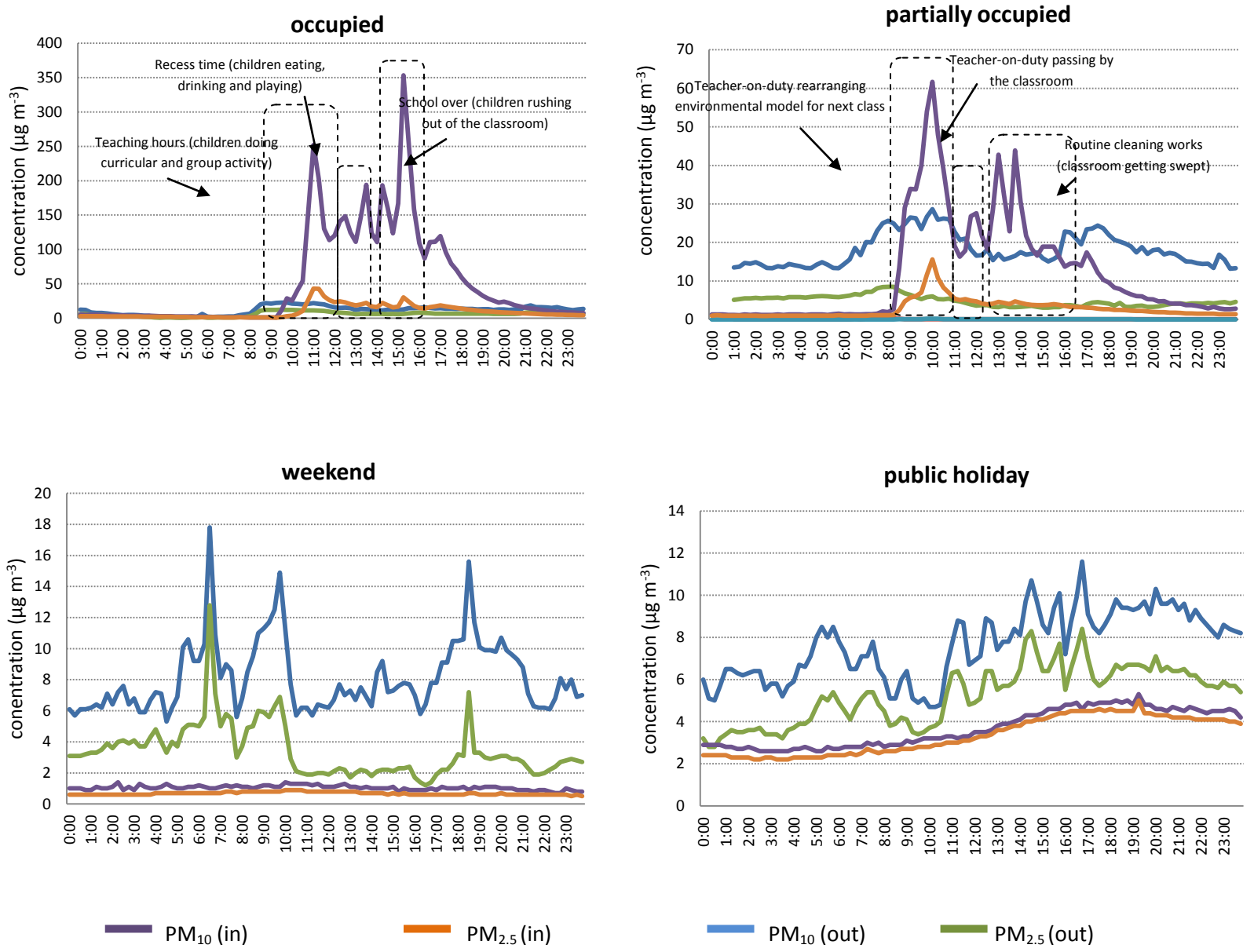
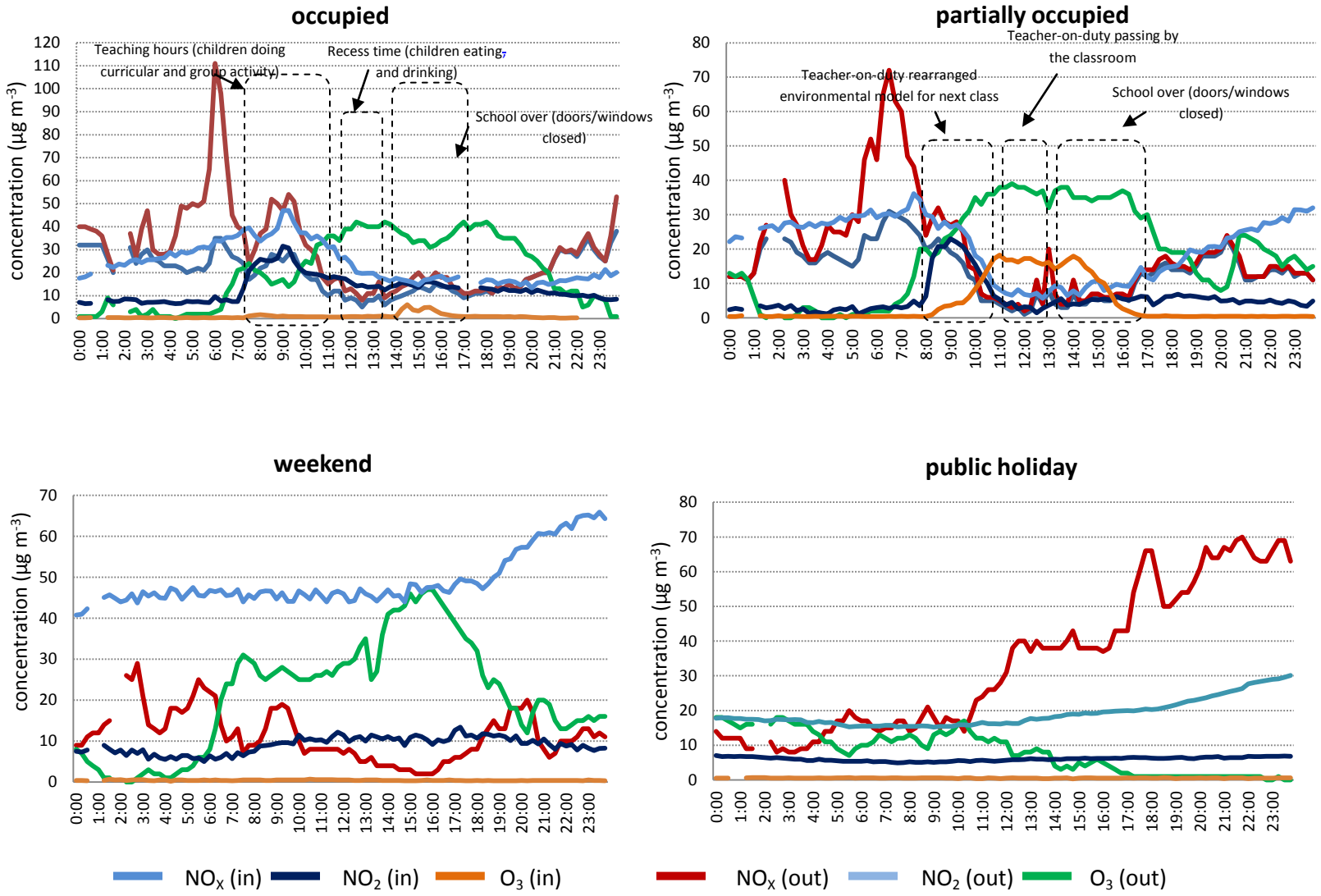


Figure 3.9: Indoor and outdoor gaseous pollutant variation profiles according to 4 time measurement periods (occupied, partially occupied, weekend and school/public holiday).



Airborne particulate matter

High levels of indoor PM_{10} and $PM_{2.5}$ concentration were observed during occupied and partially occupied periods. The fluctuation of both PM size selections were indicated by occupant behaviour. During occupied periods, from 0900-1100 hours, indoor PM_{10} concentration reached up to 250 µg m^{-3} when the classroom was used for teaching and curricular activity. Outdoor PM_{10} concentration remained constant at 30 µg m^{-3}. The level of indoor PM_{10} concentration gradually decreased to 150 µg m^{-3} during recess time, when most children and teachers spent most of the time outside in the garden. However, indoor PM_{10} concentration increased rapidlybetween 1500-1600 hours, when school was over and children rushed out from the classroom. Indoor PM concentration decreased and settled down to its minimum concentration when school ended.

Similar fluctuation patterns of indoor PM_{10} and $PM_{2.5}$ concentrationswere observed during partially occupied periods, but PM concentration levels were less than during occupied periods. Indoor PM concentration was almost at the same level at some points. The local peak of indoor PM_{10} concentration occurred around 0900-1000 hours, which may be attributed to routine cleaning works and routine checksby the teacher-on-duty to arrange environmental models for the next class.Due to the location of the classroom in between the admin office/entrance and the environmental library, the door was frequently used by people passing through to the next room. Thus, relative to these conditions, indoor PM concentrations remained elevated,ranging from 20-30 µg m^{-3} during the unoccupied period from 1200-1300 hours.During unoccupied periods (weekend and public holiday), indoor PM concentration was recorded at its minimal levels,at less than 5 µg m^{-3} for $PM_{10}$and $PM_{2.5}$. However, outdoor PM concentrationsremained constant,averaging 10 µg $m^{-3}$and 6 µg m^{-3} for $PM_{10}$and $PM_{2.5}$, respectively. Thus, it shows that the level of indoor PM concentration can vary according to school hours and different types of classroom activity patterns.

3.6 Seasonal variation

The naturally ventilated school building provides a way for outdoor pollutants to penetrate or be transported indoors. The occupants' behaviour, via closing and opening doors or windows,is regulated according to their thermal comfort and seasonal variation (Habil & Taneja 2011). Thus, it is very important to determine the characteristics of indoor-outdoor pollutant concentration through seasonal variation. This section contains two separate seasonal analyses. Seasonal correlation throughout the monitoring campaign and the differences of diurnal variation profiles between summer (June-August) and winter (December-February) were determined in order to investigate the role of opening doors or windows during those periods. It is worth noting that only the diurnal variation profile for O_3 concentration was included in this analysis, which gave the only positive output to discuss in this section.

From the results obtained in Table 3.3, the hourly mean of indoor and outdoor pollutants shows a weak correlation between seasons, with R^2 less than 0.50. This finding determined that only less than 50% of indoor pollutant concentration can be explained by outdoor sources throughout the seasons. It may indicate an independent indoor pollutant source emission inside the classroom, unaffected by seasonal variation. However, the increment of outdoor NO_X contribution indoors was observed during both autumn and winter time, while other pollutants were recorded within the same range.

Table 3.3: Indoor-outdoor linear correlation analysis by season.

Seasons	**Indoor-outdoor correlation, R^2**					**NO_2/ NO_X**
	NO_X	**NO_2**	**O_3**	**PM_{10}**	**$PM_{2.5}$**	
Autumn	0.465	0.08	0.103	0.004	0.040	0.170
Winter	0.472	0.115	0.051	0.004	0.110	0.240
Spring	0.265	0.063	0.102	0.004	0.003	0.240
Summer	0.132	0.029	0.188	0.020	0.010	0.220

NO_2/NO_Xcorrelation was analysed in this section in order to investigate the contribution of vehicle emissions inside the building. The results in Table 3.3 also show a weak correlation between $NO_2/NO_X$with R^2 less than 0.24. This finding indicates very low levels of indoor vehicle combustion, possibly contributed from a local source.

In addition, indoor and outdoor airborne particulate correlations did not show any differences between seasons. The ratios were recorded in lower values, ranging at less than 0.1. Nevertheless, a minor increment was observed in indoor $PM_{2.5}$ concentration from outdoors during summer seasons.

The diurnal variation profile was used to differentiate the effects of seasonal variation onto O_3 concentration; Figure 3.10 shows indoor O_3 concentration was observed only on weekdays during the summer. The hourly means of outdoor and indoor O_3 concentrations were 30 µg $m^{-3}$and 5 µg m^{-3}respectively. The existence of indoor O_3 during weekdays was believed to be due to outdoor O_3 penetration via opening doors and windows during summer time.

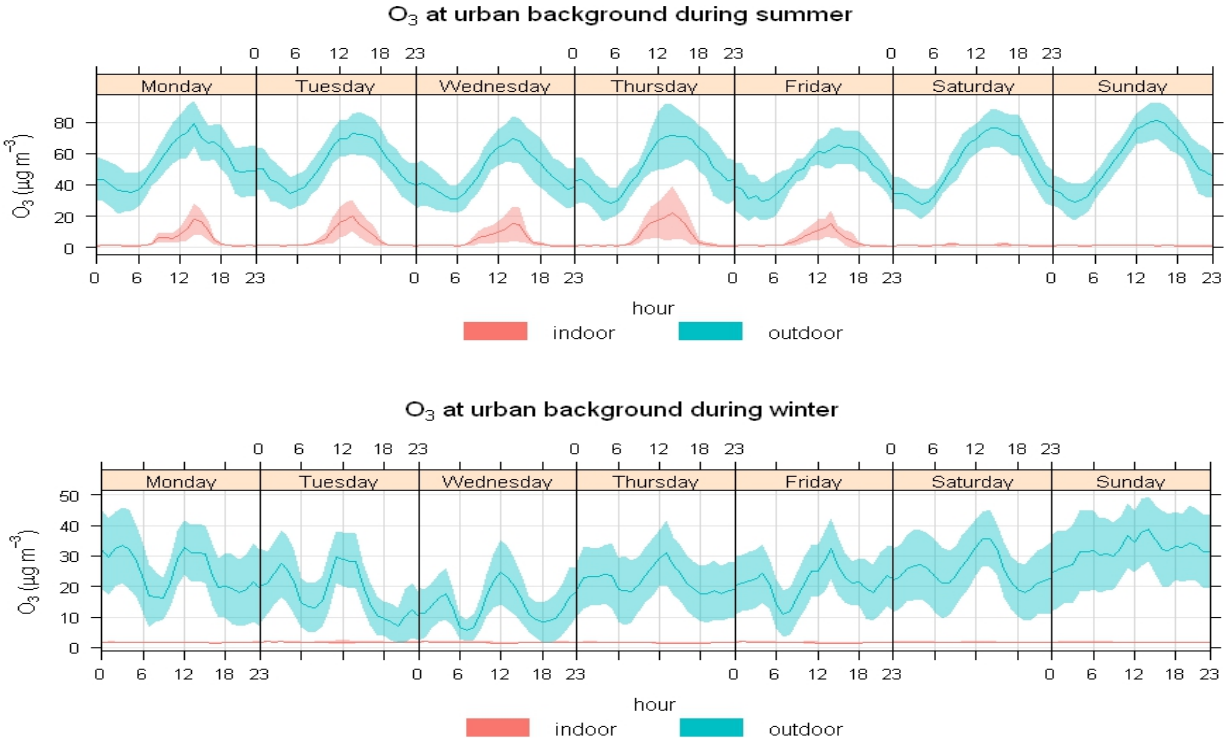


Figure 3.10: Diurnal variation profile (hourly mean) representing indoor and outdoor O_3 concentration between summer and winter time.

3.7 Discussion

Long term monitoring revealed considerable variations between indoor and outdoor concentration of gaseous pollutant species (NO_X, NO_2& O_3) and airborne particulate matter (PM_{10}&$PM_{2.5}$), which was carried out in this study for comparison purposes and for their health impacts on children. These parameters were measured simultaneously to characterise the difference as well as the dual perception of gaseous pollutant and particulate matter integrations. Further, qualitative and quantitative data monitoring analyses were conducted in order to investigate the influence of outdoor sources on indoor pollutant concentration, and/or whether independent indoor sources exist inside the naturally ventilated school building. Various factors were considered in the analyses to hypothesise the proportion of indoor and outdoor pollutants, including building characterisation (e.g. ventilation factor and building appliances), occupant behaviour, and occupancy diary activity. In addition, the monitoring dataset was analysed in short–term diurnal variation profiles according to the specified time measurement periods: occupied, partially occupied, weekends and school/public holiday periods.

Gaseous pollutant species

Generally, outdoor NO_2 and O_3 concentrations were observed to be higher than indoor concentrations. However, these concentrations were increased inside the classroom, particularly during occupied period (including partially occupied periods), as Table 3.2 shows. The outdoor NO_2 source could be partially attributed to the vehicular combustion emitted from the parking spaces in the front of the school premises. It may indicate that the increase of indoor NO_2 during rush hour was caused by a similar source when the entrance door was opened. This concentration was also observed higher during night time which possibly contributes from regional contribution. The local oxidants source has probable contributions from direct NO_2 emissions and maybe from the common-source emission of species which promote NO to NO_2conversion. This is also demonstrated by the similar pattern of higher concentration of outdoor NOX between 0500 and 0600 on weekdays, which might be strongly correlated to the regional background of ambient NO_2 concentration. Furthermore, a similar scenario also occurred with regard to indoor O_3 concentration, which was affected by ambient O_3 via opening inlets (doors and

windows). However, the indoor O_3 concentration was recorded lower than outdoors, particularly during the day. These concentrations became higher during summer. Generally, under typical atmospheric conditions, photochemistry reactions via ultraviolet light lead either to the complete conversion of all the O_3 to NO_2 with an excess of unreacted NO, or to the conversion of the entire NO to NO_2, with an excess of un-reacted O_3, as shown in Equation 3.1. In a highly polluted atmosphere, or close to an individual pollution source, the former behaviour is typically observed. Further, due to the fact that O_3 is widely distributed in the lower atmosphere, the concentration is not usually high compared to NO, hence the O_3 concentration being rapidly depleted (Lee et al. 1999).

$$\mathbf{NO + O_3 = NO_2 + O_2} \qquad \textbf{Equation 3.1}$$

In the ambient environment, NO and NO_2 are the major gaseous species in the production and destruction of O_3. However, in indoor microenvironments with insufficient UV light, the majority of O_3 existing indoors was attributed from outdoor penetration (via windows, opening doors or ventilation systems) (Zuraimi et al. 2007, Weschler 2011). Two studies in residential areas from multiple locations in California and New Jersey demonstrated indoor O_3 varied with outdoor concentration in similar patterns (Zhang & Lioy 1994). These studies also suggested that the elevation of indoor O_3 significantly correlated with air exchange rates at home. Due to the rapid reaction of O_3 (sun light radiation), indoor O_3 is particularly prevalent during the summer season. A school study in Belgium revealed the seasonal ambient environment influenced indoor NO_2 and O_3 inside the classroom. However, due to differences of deposition velocities and decomposition rates in indoor air, indoor-outdoor ratios of the gases decreased in the sequence NO_2, SO_2 and O_3(Stranger et al. 2009).

The hourly mean variation profile, as shown in Figure 3.3, also supports this finding. Rapid increments of indoor NO_X, NO_2 and O_3 during rush hour (0800-0900) were observed due to outdoor contribution via doors and windows being opened when school starts. However, why indoor NO concentration decreased during rush hour (morning and evening time) is still questionable. A similar pattern of high concentration of indoor NO_X which was mainly contributed from NO concentration,was recorded during unoccupied

periods (night time and at the weekend), remaining at a constant concentration of about 25-40 µg m^{-3}. Therefore, it may indicate that an independent NO source exists indoors;however, despite thorough investigation, the actual source was never identified properly in this study. There are a few assumptions via virtual inspection made during site visit to double check the possible source of NO_X or NO source, which might leaked from boiler or heating system. From indoor-outdoor source prediction analysis as stated in Appendix A, in the Figure A.4, the results shows indoor NO was higher than outdoor NO concentration when heating system was activated during occupied/partially occupied period. Further, those concentrations were at the same concentration when the heating system was switched off, particularly during public holiday. However, this finding was not considered as absolute conclusion since it requires further inspection particularly for the whole heating system in detailed and other technical aspects.

Indoor and outdoor ratio analyses in Figure 3.5 also showed similar findings. A higher I/O NO ratio recorded almost 8.0 at the weekend, followed by partially occupied and occupied periods recording about 6.0 and 5.0, respectively. Ironically, the lowest I/O NO ratio was observed during public holidays, mainly during Christmas break. It may indicate that the independent indoor NO source was terminated temporarily during this time. Additional analysesin this study examined the influence of meteorological factors in order to correlate with other analyses. Even though this building is naturally ventilated, the results from Figure 3.5 did not show any contribution of meteorological factors (including wind speed and wind direction) into transportation of outdoor gaseous concentrations indoors.The absence of local meteorological station and also air exchange rates, which are not included in this study, might be useful to consider in order to fully understanding the transfer of outdoor pollutants indoors. Murray & Burmaster (1995) stated in their study that improving the air tightness of a building protected it from outdoor source penetration, which was driven by the air exchange rate. The penetration of outdoor elements indoors depends on the opening of inlets (e.g. window and doors), connected to occupant behaviour due to thermal comfort and seasonal variation.

Particulate matter

The long term indoor-outdoor PM monitoring variation profile in Figure 3.4 showed a different concentration pattern when compared to gaseous pollutant species. The results obtained in this study showedthat particle concentrations during occupancy are higher than those outdoors when the classroom was unoccupied. The building occupancy and suspension of larger particles were believed to be significant contributors to the local indoor source inside the classroom.

Ambient air quality standards and indoor air quality guidelines (WHO and USEPA) have been established recently to define maximum concentrations allowed in ambient and indoor microenvironments to protect human health from air pollution hazards. Indeed, the indoor average of PM_{10}concentration during occupied periods in this study demonstrated that the daily mean indoor PM_{10} concentration exceeded the WHO guidelines, which have been set at 40 µg m^{-3},while outdoor PM_{10} concentrations remained below the guidelines, set as 50 µg m^{-3}. Also, a number of $PM_{2.5}$ concentrations during periods where the classroom was occupied exceeded the indoor limit (15 µg m^{-3}).

A recent study, conducted in a three-storey naturally ventilated school building in close proximity to an urban roadway and surrounded by a residential area (Goyal & Khare 2009), showed the occupants' activities in the classroom and movement indoors either tended to resuspend the particulates or delay their deposition/settling, resulting in increased indoor PM concentrations. Furthermore, another investigation inside a naturally ventilated school building carried out for PM_{10} concentration reported that a significant increment of PM_{10} was observed to be higher when the classroom was occupied compared to when it was unoccupied –during the holiday period (Triantafyllou et al. 2008).

On the other hand, the increment of fine particles in this study might be explained by the opening of inlets (e.g. doors and windows)due to occupant behaviour,particularly during occupied periods. The changes in building condition due to the opening of doors/windows led to an increase in air change, possibly increasingthe concentration of indoor fine particles ($PM_{2.5}$)via outdoor penetration. Even though there is no specific air

exchange rate investigation in this study, a previous study proved that the correlation between indoor and outdoor is much stronger, particularly for $PM_{2.5}$ and PM_1 (R^2 = 0.96 and 0.92, respectively) by the opening of inlets. This was due to opening windows and allowing outdoor particles to enter the classroom(Alshitawi & Awbi 2011). Higher penetration efficiency for larger particles was also demonstrated in other studies (Fromme et al. 2007, Branis & Safranek 2011, Branis et al. 2011). Indeed, Guo et al. (2008) concluded that the penetration efficiency decreased with increasing outdoor particle number concentration. They discovered that when the outdoor particle number concentration increased, there was an associated increase in the concentration of fine particles, which have been demonstrated to have higher deposition rates and lower penetration efficiencies.

In addition, monthly variation profiles in Figure 3.4 showedthat the indoor PM_{10} was always higher compared to outdoor concentration throughout the year. The highest indoor concentration was recorded during the winter period for both PM size ranges; however, indoor concentration dropped equivalent to outdoor concentrationduring summer time. This may indicate a similar issue of outdoor penetration when windows and doors were frequently opened. This finding is consistent with another recent study by Habil & Taneja (2011). During winter, mean indoor PM_{10}, $PM_{2.5}$ and PM_1 concentrations ranged up to 497, 220, 135 µg m^{-3}, which lowered to 3, 3 and 2 times, respectively, in summer as compared to winter.

I/O ratio is often applied to detect the presence of indoor sources, usinga ratio above 1.0 (e.g.Poupard et al. 2005). The I/O ratio analysis in Figure 3.6 demonstrated that as the particle size range increased, the occupancy ratio also increased. It may indicate that the larger particles have a strong relationship with occupancy activity/behaviour. This finding is supported byBranis et al. (2005), who showed the ratio between indoor and outdoor PM_{10} exceeded unity (1.07) during the day on workdays when the classroom was occupied by students. I/O ratios for all PM size ranges during unoccupied periods were recorded lower than 1.0, which is consistent with this study. The absence of people resulted in average ratios of 0.60, 0.56, and 0.50 for workday nights, weekend nights and weekend daytime, respectively. The ratios obtained in this study were higher as compared

to their study. This could be due to the difference in the number of occupants and their activity, causing greater suspension and delay in settling PM.

Diurnal variation profiles in this study were analysed on a short-term basis using different time measurements (occupied, partially occupied, weekend and public holiday). Local peak indoor PM concentration was identified in this analysis in order to determine theinfluence of occupants' activity in the classroom (Figure 3.8). The influence of student attendance and occupant activity on PM_{10} in this study was very clear; hourly mean differences between occupied and unoccupied periods were about 100 times higher than when the classroom was unoccupied. This finding agrees with a previous study by Parker et al. (2008), which stated that when the building was occupied the indoor coarse particle count was much higher than ambient concentrations. This study also concluded that staying inside a mechanically ventilated building reduces exposure to outdoor submicron particles. However, Guo et al. (2008) mentioned in their study that the indoor $PM_{2.5}$ concentration was mainly affected by the outdoor source ($r = 0.68$, $p < 0.01$), whereas the indoor particle number concentration had some association with outdoor particle number values ($r = 0.66$, $p < 0.01$), even though the indoor particle number concentration was occasionally influenced by indoor sources.

3.9 Conclusion

In this study, the relationship between indoor and outdoor pollutant concentrations was analysed in order to estimate the proportion, behaviour and mechanisms dictating the transport of outdoor pollutants into the naturally ventilated classroom. Typically, air movement within naturally ventilated building envelopes is determined by opening doors and windows; air exchange rate (AER) provides the proportion of internal and external air inside buildings. However, the widely variable building use in long-term measurement means that this would have limited application. For examples, the rapid changes and inconsistency of ventilation rates depending on the specific building use will affect the concentration of NO_X, O_3 and PM differently. On the other hand, the presence of indoor NO source was believes to play important role of reducing O_3 in the classroom. However, this finding may not be applicable to other naturally ventilated buildings that have no such source.

Chapter IV

Case study 2 – I/O transfer of pollutants in a mechanically ventilated office building adjacent to a busy road

4.1 Introduction

The relative contributions of outdoor pollutant penetration and indoor sources are considered major concerns of IAQ exposure; several studies have shown high outdoor pollutant exposure in buildings due to their close proximity to major traffic emissions (M. Jamriska 1999, Ni Riain et al. 2003, Poupard et al. 2005, Goyal & Khare 2009). The majority of these studies were based on short term measurement campaigns. However, a long term measurement time series is important in order to correlate the different types of pollutant species from both internal and external sources. Building use, street canyon effects and meteorological conditions such as wind direction/speed are major factors influencing the transport of external pollutants into a building, particularly in urban buildings adjacent to a busy road.

A mechanically ventilated office building located adjacent to a busy road was chosen in this study to represent the 'worst' exposure scenario that typically arises in most office buildings in London. This site monitoring campaign was selected to complement measurements undertaken at an urban background location in London in order to compare two extreme exposure scenarios. The findings from this study may potentially be used to describe indoor air quality due to a variety of impact factors, including outdoor environment (road with heavy traffic), building orientation, and building ventilation and occupancy.

4.1.1 Site sampling and description

Site selection, measurement methods and protocols are described in Chapter II, section 2.2.

An office building situated in the heart of Greater London near Upper Thames Street, to the east of the River Thames was chosen for this study. The building facade is 2.5m from the kerb of a heavily trafficked road. Congestion is common and at peak periods long queues can form stretching the entire length of the street, with queuing more predominant when traffic is stopped by a light. Upper Thames Street in front of the building has street canyon characteristics (i.e. a narrow width of approximately 20m, and a high building height of about 150m); as a result, pollutant concentrations at this location are often elevated. The indoor and outdoor pollutant measurements were made in a 1500m^2 room in the main entrance reception area. The main entrance to this building was in normal use with variable occupancy and without any typical pollutants from office usage (e.g. printing machine emissions) and with a non-smoking policy. The room served as a reception, with at least one reception staff on duty, and operated from 0800 until 1800 hours from Monday until Friday, closed during non-working hours and weekends.

The main entrance was built with a typical high ventilation air condition (HVAC) system with filtration and variable-volume makeup air. Systematic tubing exhaust was controlled by the main HVAC inlet on the roof of this building. The air-tightness condition in the main entrance area was affected via automatically opening entrance doors. The gaseous measuring equipment was placed on a table in the small sealed room within the main entrance area.The sampling inlet position and reception area floor map are illustrated in Chapter II. In detail, the outdoor sampling inlet was installed at the top outside ceiling, about 1m from kerbside; the indoor inlet was located near the reception desk. Sampling heights were within 2-3m of the ground. An indoor PM monitor was also installed within the same area. Due to some difficulties dealing with electricity supply and safety issues, a similar monitor for measuring outdoor airborne PM was impossible to install at this site. An external data source was used in this study to compare indoor PM monitoring. The description of external PM measurement will be described in this chapter.

4.1.2 Research aims and objectives

The aims and objectives were identified and have been assessed similarly to previous chapter, except it was differed according to location and building types. The main objectives of this chapter are as follows:

a. The differences of indoor-outdoor pollutants concentration according to the long term diurnal variation profiles.
b. The differences of indoor-outdoor pollutants concentration according to meteorological condition (wind speed and wind direction).
c. The differences of indoor-outdoor pollutants concentration according to building use under different time measurement scenarios (occupied, partially occupied, weekend and public holiday).
d. The differences of indoor-outdoor pollutants concentration according to the seasonal variation.

4.2 Long term indoor-outdoor monitoring database

Methods of data capture, ratification and data management for this study are described in Chapter II, section 2.4. Monitoring at this site ran from August 2008 until March 2011. However, due to difficulties dealing with electricity supply and safety issues, indoor PM monitoring using an OSIRIS monitor ran from February until March 2011. External PM_{10} data was taken from an existing TEOM instrument located about 200m away. The problems relating to the use of different sampling techniques to compare indoor and outdoor PM_{10} are discussed in Chapter II, section 2.5. As shown in Table 4.1, indoor-outdoor gaseous pollutant monitoring achieved greater than 90% valid data.

Table 4.1: Monitoring data summary statistics from mechanically ventilated office building.

Pollutant species	Sampling inlets	Mean (µg m^{-3})	95 percentile (µg m^{-3})	Capture Rate (%)
NO_X	Indoor	363.8	1005.6	96.6
	Outdoor	434.4	1240.4	99.6
NO_2	Indoor	101.5	168.9	96.6
	Outdoor	127.1	218.5	99.6
PM_{10}	Indoor	21.7	57.3	89.6
	Outdoor *	39.8	75.7	90.4
$PM_{2.5}$	Indoor	7.1	17.5	89.6

Notes:Monitoring data of gaseous pollutants (NO_X and NO_2) were captured from August 2008-March 2011, whereas data for particulate matter (PM_{10} and $PM_{2.5}$) were captured from February-March 2011.

Generally, indoor and outdoor hourly mean NO_X and NO_2 concentrations were relatively high compared to other roadside monitoring in London; for example, period mean outdoor NO_X was 434.4 µg m^{-3} and indoor NO_X was 363.8 µg m^{-3}. Indoor NO_2 concentration exceeded the WHO Limit Value (200 µg m^{-3} hourly mean) on 11 occasions in 2008 (866 µg m^{-3}), and it failed the EU directive obligations set for outdoor pollution in 2009 (mean was 951 µg m^{-3}), 2010 (mean was 646 µg m^{-3}) and 2011-to date (mean was 231 µgm^{-3}). Furthermore, Upper Thames Street was determined to be the highest polluted street in London, considered a 'hotspot' (Defra, 2011; Campaign for Clean Air in London, 2011).

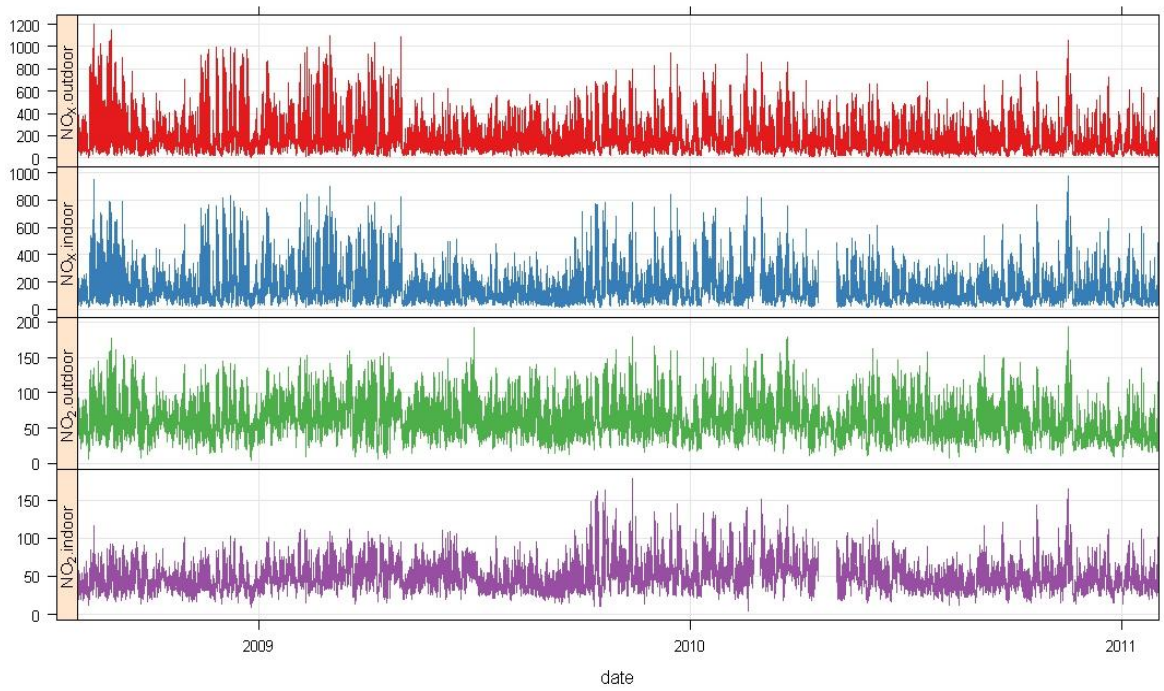


Figure 4.1: Time series plot for indoor-outdoor gaseous pollutants monitored from August 2008-March 2011.

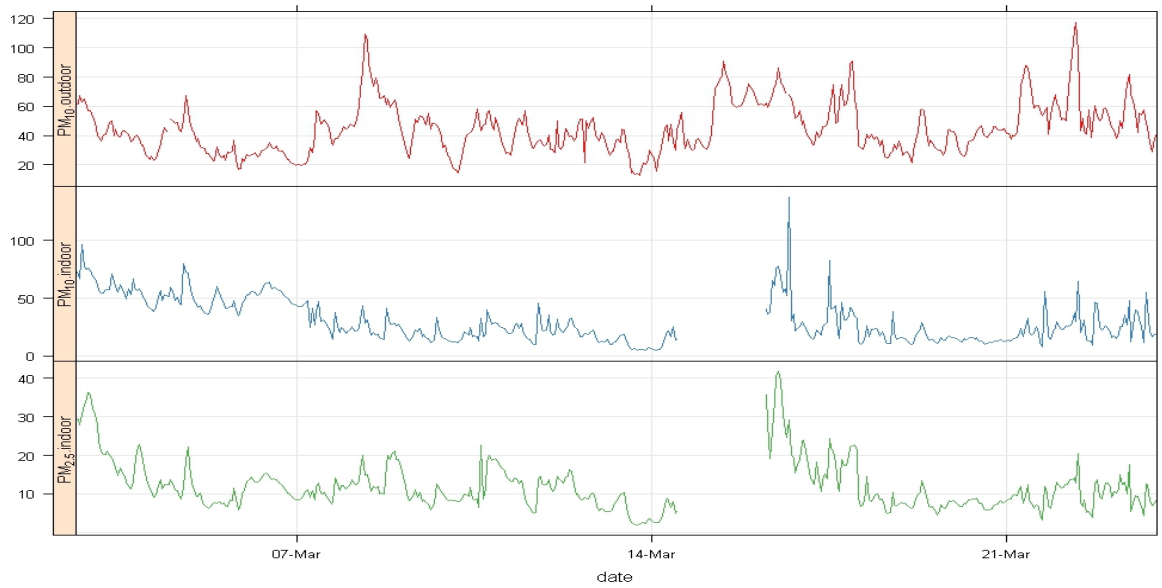


Figure 4.2: Time series plot for indoor-outdoor particulate matter monitored from February-March 2011.

Notes:*Each of the pollutant parameters in both of figures above were in different scales in caption.*

4.2.1 Diurnal variation profile

4.2.1.1 Indoor-outdoor gaseous pollutants (NO_X and NO_2)

The diurnal NO_X and NO_2 variation profiles, as shown in Figure 4.3, describe three different mean scale periods: hourly mean (24 hour average plot), weekly mean (daily mean plot on a weekly basis), and monthly mean (12 month plot). Data processes and output analyses were produced using R statistical package software.

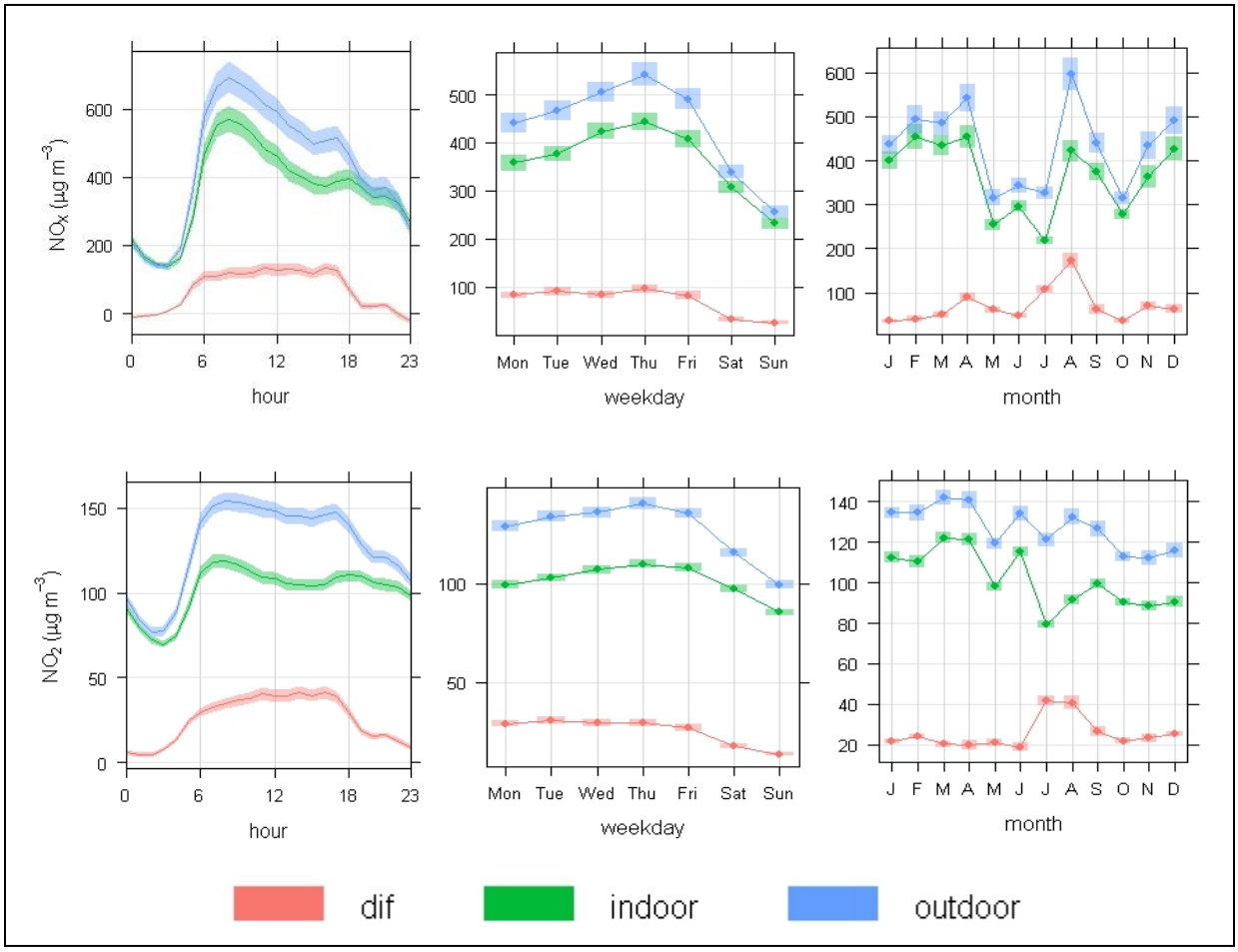


Figure 4.3: Diurnal variation profile (hourly-weekly-monthly) for indoor-outdoor NO_X and NO_2, mechanically ventilated office building.
Notes: Additional information on concentration differences between indoor and outdoor NO_X and NO_2 also included in this figure.

Hourly variation profile

Generally, the hourly mean concentrations from both external and internal measurementshad similar diurnal profiles, as illustrated in Figure 4.3. In detail, between 0000 and 0400 hours, indoor and outdoor $NO_X$and NO_2 were observed at the same concentration (averaging 180 µg m^{-3} for $NO_X$and 80 µg m^{-3} for NO_2). However, at 0500 hours, both NO_X and NO_2 concentrations rapidly increased to their peaks at 0800 hours (700 µg $m^{-3}$and 160 µg m^{-3} outdoor $NO_X$and NO_2, 500 µg $m^{-3}$and 120 µg m^{-3} indoor $NO_X$and NO_2 respectively), coinciding with the increase in rush hour traffic on the adjacent road. Additional building use factors, such as the main entrance doors being opened by staff entering the building during rush hour, may have contributed to indoor concentrations due to outdoor pollutant penetration. Further, the role of the ventilation system (activated during working hours) to expel internal pollutant concentration was observed during these hours. The pattern of concentrations dropped during working hours; from 0900-1800 hours, outdoor $NO_X$and NO_2 concentrations wereobserved to be higher compared to indoor $NO_X$and NO_2, but both pollutant concentrations were always following each other. It worth noting that a small positive increment at about 1700 hours may also have been driven by building use factors, i.e. increased traffic flow and the staff rushing out from the building after working hours.

During the unoccupied period from 1800-2300 hours except a small positive increment at 1700 hours, indoor-outdoor NO_Xconcentrations were reduced from 550 to 250 µg m^{-3} and reached to almost at the same concentration, whereas outdoor NO_2 was still higher compared to indoor NO_2 (averaged 120 µg m^{-3} outdoorsand 100 µg m^{-3} indoors). Interestingly, indoor NO_2 concentration is remained at its concentration as observed during office hours. During this period the main entrance was closed and the ventilation system was de-activated. This pattern of concentration may possibly be explained by the lack of ventilation and outdoor sources infiltrating the building.

Weekly variation profile

In general, on weekday observation (Monday to Friday), daily mean, outdoor NO_X and NO_2 were higher compared to indoor $NO_X$and NO_2 (480 µg $m^{-3}$and 130 µg m^{-3} for outdoor $NO_X$and NO_2, 380 µg $m^{-3}$and 100 µg m^{-3} for indoor $NO_X$and NO_2). Daily mean concentrations dropped at the weekend, to mean 280 µg m^{-3} and 110 µg m^{-3} for outdoor $NO_X$and NO_2, and 260 µg $m^{-3}$and 90 µg m^{-3} for indoor $NO_X$and NO_2, respectively. There was less difference between indoor and outdoor concentrations at the weekend as compared to weekdays. This finding was very important, showingthatnegative pressure occurs when the mechanical ventilation system was de-activated and that the inverse pressure within the building envelope may increase the transferring of outdoor pollution indoors.

Monthly variation profile

In one year of observation, monthly mean concentrations were observed to be higher outdoors. Nevertheless, the levels of concentration between indoor-outdoor NO_X and NO_2 were always following each other. This supports the finding that concentrations indoors were driven by outdoor traffic sources to the same degree throughout the year.

4.2.1.2 Indoor-outdoor PM (PM_{10}& $PM_{2.5}$)

Indoor PM airborne concentration from two selective size fractions (PM_{10} and $PM_{2.5}$) was monitored simultaneously alongside gaseous pollutant species. In general, PM airborne concentration had different patterns of concentration when compared to gaseous variation profiles, as shown in Figure 4.4. Most of the local indoor peak PM concentration was driven by building occupancy, as discussed below.

Hourly variation profile

Indoor PM was observed at a constant concentration (averaging 18 µg $m^{-3}$and 2.5 µg m^{-3} for PM_{10} and $PM_{2.5}$, respectively) at 0000-0400 hours, during the unoccupied period. Peak indoor concentration was recorded during rush hour, from 0500-0900 hours, reaching up to 40 µg m^{-3}(PM_{10}) and 12 µg m^{-3}($PM_{2.5}$). Indoor PM concentration then

decreased during working hours (0900-1800), after which it increased again and reached its highest concentration, at 80 µg $m^{-3}$and 12 µg $m^{-3}$for PM_{10} and $PM_{2.5}$ respectively. As peak indoor concentrations were anomalous and, in the case of the afternoon peak, higher than outdoor concentrations, it is most likely that PM suspension via occupier movements was the main factor producing these peaks in indoor source PM.

Unlike the NO_X measurements, outdoor PM_{10} concentrations did not closely track indoor PM_{10} concentrations. Outdoor PM_{10} concentration increased during rush hour and remained at a constant concentration average of 40 µg m^{-3}.

Weekly variation profile

Overall, mean indoor PM_{10} was lower compared to outdoor PM_{10} (24 µg m^{-3} and 40 µg m^{-3}, respectively) from Monday to Friday. Indoor PM_{10} and $PM_{2.5}$ concentrationsdecreased throughout the weekend. This finding supports the hypothesis that building occupancy via occupier movements as well as penetration factors contributed to indoor concentration. Without any indoor source or occupancy issue, the level of indoor PM concentration remained at minimal concentration at the weekend. Outdoor PM_{10} also decreased, linked to reduced traffic flows at the weekend.

Monthly variation profile

No monthly profile was produced due to the short monitoring period.

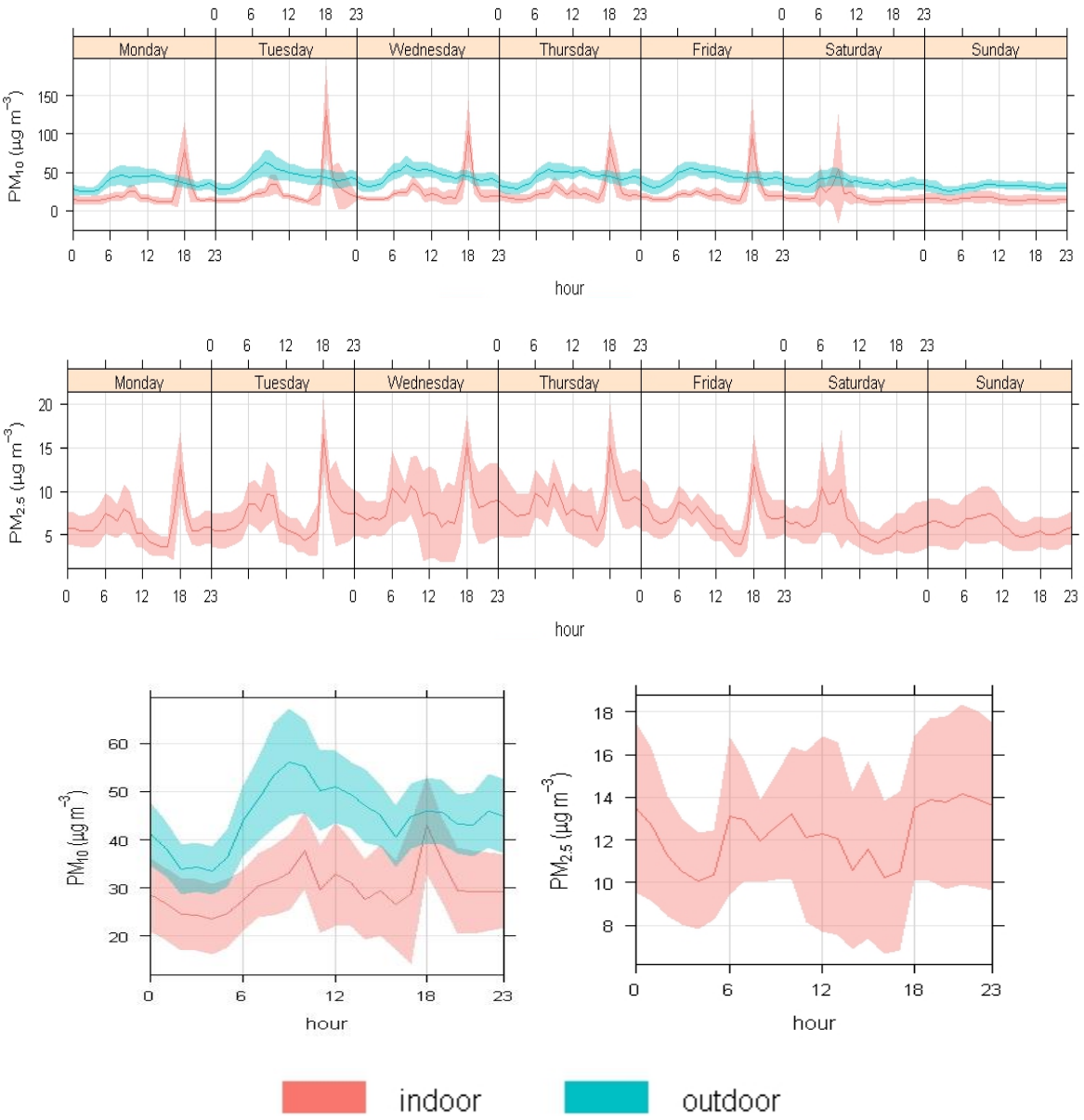


Figure 4.4: Diurnal variation profile (hourly-weekly-monthly) for indoor-outdoor $PM_{10}$and indoor $PM_{2.5}$ at mechanically ventilated office building.
Notes:Outdoor PM_{10} was captured from local LAQN site measured by PM_{10} TEOM.

4.3 Meteorological conditions

The significant amount of pollutants originating from vehicle combustion sources and their dispersion in a street canyon is an important factor (Bady et al. 2011, Zhang et al. 2011). The street canyon effect at this site was caused by the combination of a narrow street (Upper Thames Street) and tall buildings which line it continuously along both sides. The main assumption of this street canyon dispersion model considers wind flow distribution; this phenomenon usually includes high circulated air movements and building orientation. Thus, the pollutant distribution in urban street canyons is mainly diluted by canyon geometry and local meteorological conditions including wind direction and wind speed.

Polar frequency plot

The characteristics of pollutants at this site were analysed to consider the influence of wind direction and speed. R statistical software was used to produce polar frequency plots to illustrate mean pollutant concentrations associated with binned wind direction and wind speed measurements. For a description of how polar frequency plots are produced in R, see Carslaw and Ropkins (2011). Meteorological data from Bexley 2 (BX 2) were chosen for this analysis; this site was identified in previous reports (Defra, 2011) to represent regional atmospheric conditions which derived from a homogenous local source within the study site.

The colour scale contrast between indoor-outdoor gaseous pollutants in Figure 4.5 shows that the hourly mean NO_X and NO_2 had similar distributions. While outdoor NO_X and NO_2 concentrations were higher than indoors, the distribution of concentrations over all wind speeds and directions was very similar. The highest outdoor NO_X and NO_2 concentrations arose during winds with a southerly component, when emissions from the adjacent road were blown towards the study building, having been re-circulated by the canyon effect (road orientation is shown by a dashed red line). This analysis provided further evidence that emissions from the adjacent road were the dominating source of NO_X and NO_2 pollution inside the building.

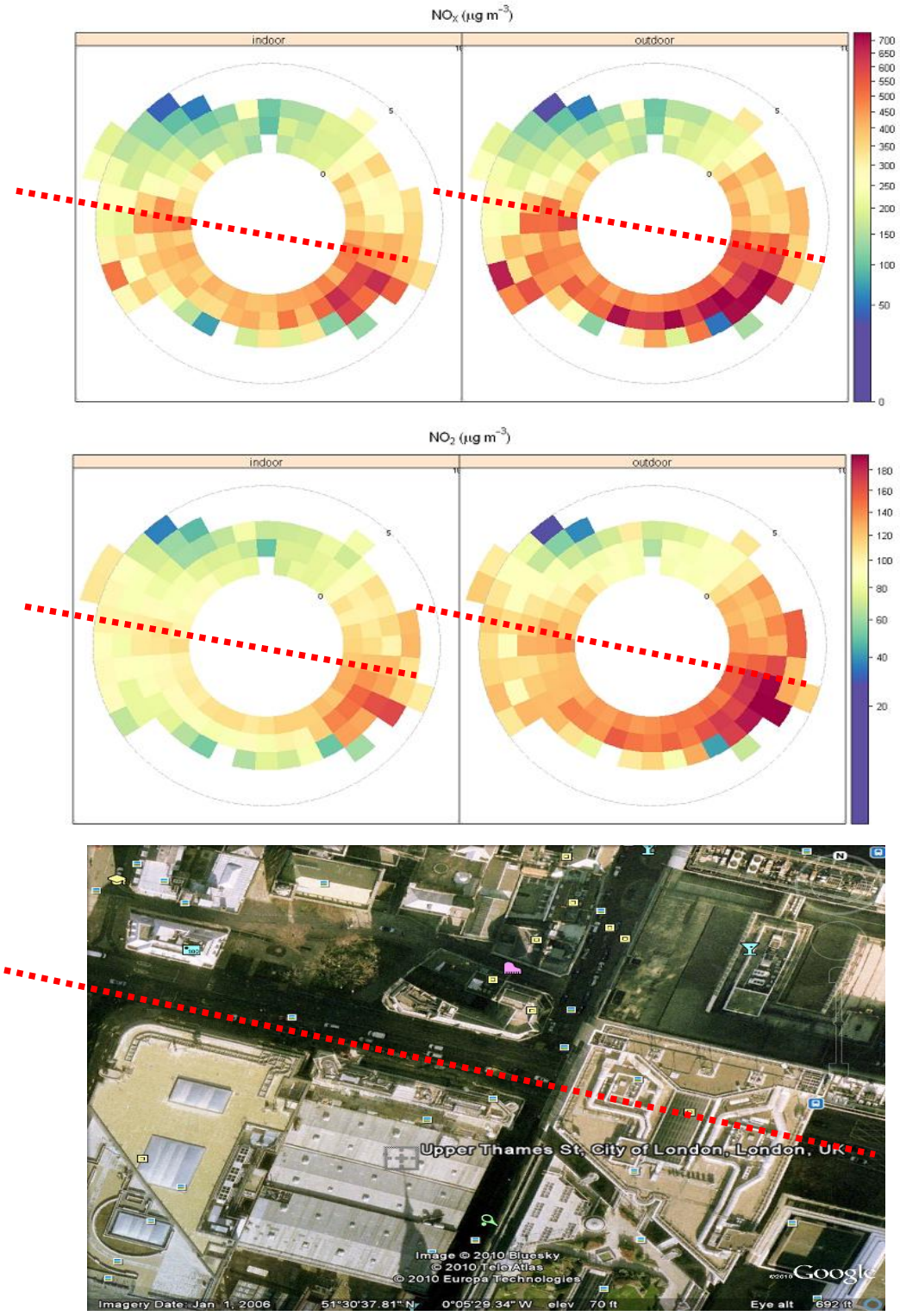


Figure 4.5: Polar frequency plot between indoor-outdoor $NO_X$and NO_2 concentrations, mechanically ventilated office building. The dashed line indicates the orientation of the adjacent road (Upper Thames Street).

Notes:Colour contrast represents pollutant concentrations in µg m^{-3}. Dotted red line shows roadside orientation at the north side of the mechanically ventilated office building.

4.4 Building occupancy: Indoor-outdoor monitoring data comparison

In order to ascertain the influence of building occupancy on pollutant concentration, the monitoring data obtained during the course of the one year (gaseous pollutants) and 90-days (PM) measuring campaigns were divided into three separate periods:

a. Occupied weekday: 0700 – 1800 hours.
b. Unoccupied weekdays: 1900 – 0600 hours.
c. Unoccupied weekend (Sunday).

Indoor-outdoor (I/O) Ratio Analysis

The aim of this analysis was to predict indicators for the strength of indoor sources, which could highly vary depending either on building occupancy or the transport of outdoor pollutants indoors. Figure 4.6 shows the ratio mean distribution with standard deviation representing I/O ratio according to the three different time periods.

The I/O ratio of NO_X and NO_2 was significantly higher during the unoccupied period, $p < 0.05$. Most I/O ratio values were close to 1.0, indicating that a high proportion of indoor NO_X and NO_2 were due to outdoor sources when the building was closed and empty. However, the I/O PM_{10} ratio was slightly higher during occupied periods, with significant differences ($p < 0.05$) when compared to the weekend period. This finding may suggest that with the absence of indoor PM sources, outdoor PM may infiltrate the main entrance of the building.

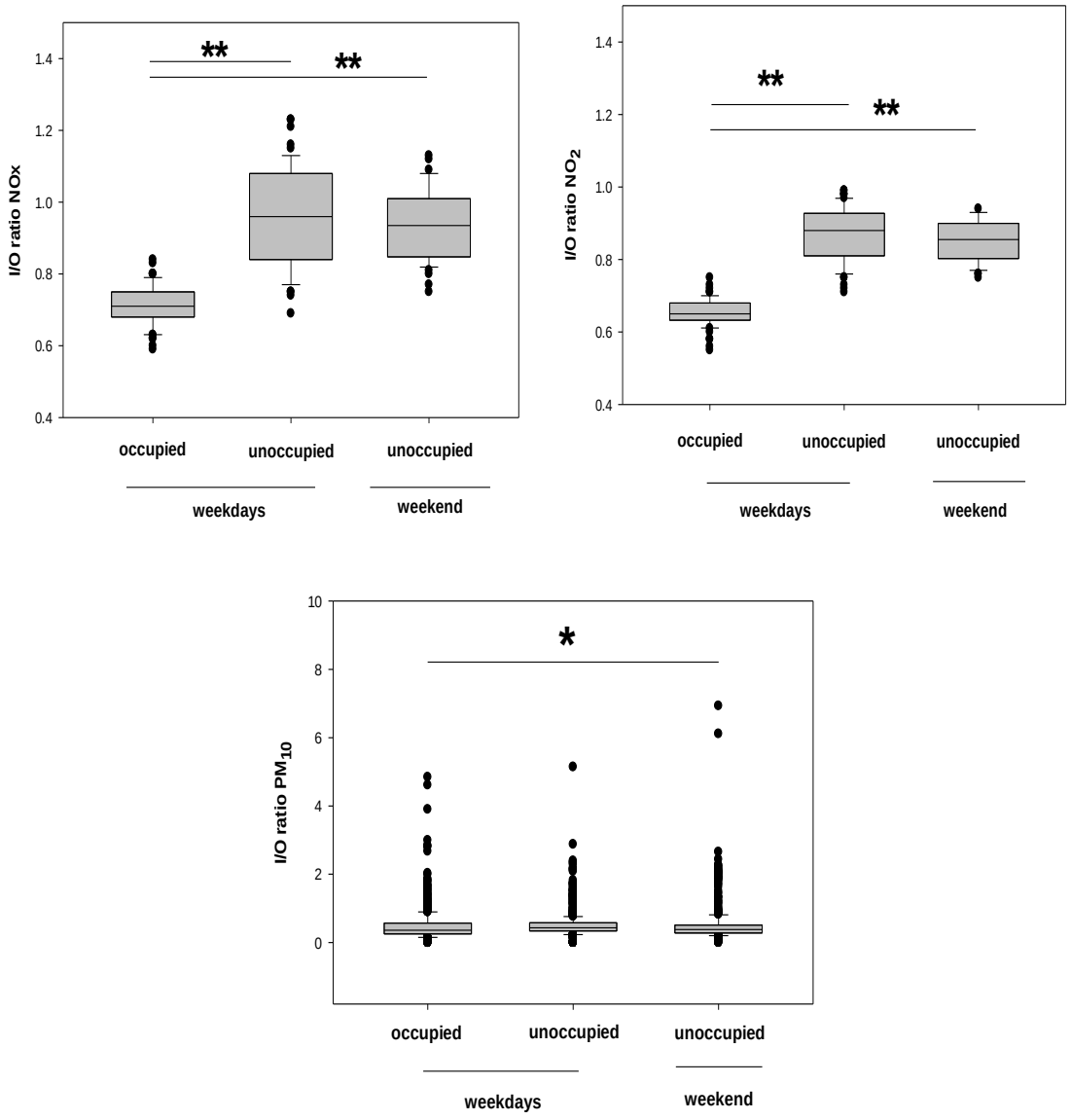


Figure 4.6: Distribution of I/O ratio of indoor and outdoor pollutant species at mechanically ventilated office building.
*Notes: Statistical comparisons according to building occupancy were analysed using a one way ANOVA, with post hoc Tukey analysis. Data marked with an * and ** indicate significant differences, with $p < 0.05$ and $p < 0.001$, respectively.*

Indoor-outdoor Correlation (I-O) Analysis

The source of the relationship between indoor and outdoor pollutants can be implied by looking at the correlation between these two sources. I-O values were determined to view the dependency of indoor pollutants on their corresponding outdoor concentration. In addition, NO_2/NO_X analyses were used in order to correlate the gaseous pollutant concentrations in determining vehicle combustion sources (Carslaw 2005, Carslaw & Beevers 2005).

Generally, the I-O for $NO_X$was higher during the unoccupied period, particularly at the weekend, with an I-O value of 0.98. NO_2 was similar, with the results showing a strong correlation at the weekend, I-O value 0.95. However, there is no evidence to show any significant correlation between indoor and outdoor PM concentration in all three measurement periods. Further, NO_2/NO_X values show a significant contribution of vehicle derived combustion inside the building, particularly during working days (day and night), with NO_2/NO_X value 0.98 ($p < 0.05$).

These results suggest that higher ratios and correlations between indoor-outdoor NO_X, NO_2 and PM_{10} during unoccupied periods show significant contributions from outdoor sources. Notably, the reduction of traffic combustion and its contribution was not observed due to the similar range of NO_2/NO_X ratios at the weekend (0.98, $p < 0.05$).

Table 4.2: Correlation coefficients between indoor and outdoor pollutant species at mechanically ventilated office building.

Pollutant species	**Workday – day (occupied)**	**Workday – night (unoccupied)**	**Weekend (unoccupied)**
NO_X in/ NO_X out	0.94 **	0.96 **	0.98 **
NO_2 in/ NO_2 out	0.75 **	0.95 **	0.95 **
PM_{10} in/ PM_{10} out	0.07	0.36	0.29
NO_2/ NO_X	0.98 **	0.98 **	0.98 **

*Notes: workday (Mon-Fri) and weekend (Sat-Sun), day (0700-1800) and night (1900-0600), significant p-value (less than 0.05 **)*

Time-lag Correlation Analysis

The speed of NO_2 transport into the building was analysed by repeating the correlation analysis with different time lags. A 15-minute average time lag was used in this analysis. The highest correlation was achieved in first 15-minutes of lag (as shown in Table 4.3). The correlation values for both pollutants NO_X and NO_2 were reduced when lag time was analysed further until lag 10 (data not shown).

Table 4.3: 15minute time lag correlations between indoor-outdoor $NO_X$and NO_2 concentrations, mechanically ventilated office building.

Gaseous pollutant	**15 mins lag**					
	0	**lag1**	**lag2**	**lag3**	**lag4**	**lag5**
	R^2	**R^2**	**R^2**	**R^2**	**R^2**	**R^2**
NO_X in/ NO_X out	0.85	***0.88***	0.82	0.77	0.72	0.66
NO_2 in/ NO_2 out	0.67	***0.68***	0.64	0.60	0.57	0.54

4.5 Seasonal variation

The building's location at a roadside site provides a way for vehicle combustion or other local pollutant sources to penetrate indoors. Central heating and temperature adjustment on the mechanical ventilation system also differed according to occupants' thermal comfort and seasonal variation. Indeed, the temperature differences may reflect the negative-positive pressure to initiate indoor and outdoor pollutant interchange concentration within the building envelope. Thus, the difference in diurnal variation profiles between seasons is compared in this analysis in order to hypothesise those effects. There are two seasons involved, summer (June-August) and winter (December-February). The differences between hourly means from both indoor and outdoor pollutant concentrations were plotted in weekly variation profiles as illustrated in Figure 4.7.

From the results obtained, it is noticeable that the hourly means of outdoor NO_X and NO_2 concentrations in summer were slightly higher than those monitored in winter. In summer, the difference between indoor-outdoor NO_X and NO_2 was 140 µg $m^{-3}$and 40 µg m^{-3}, respectively. However, these differences in concentrations slightly fell to a mean value of 120 µg m^{-3} (NO_X) and 20 µg m^{-3} (NO_2). Further, in daily profile comparison, the patterns of different concentrations of NO_X and NO_2 for both seasons were observed almost in a similar pattern to diurnal variation profiles, as discussed in previous analyses.

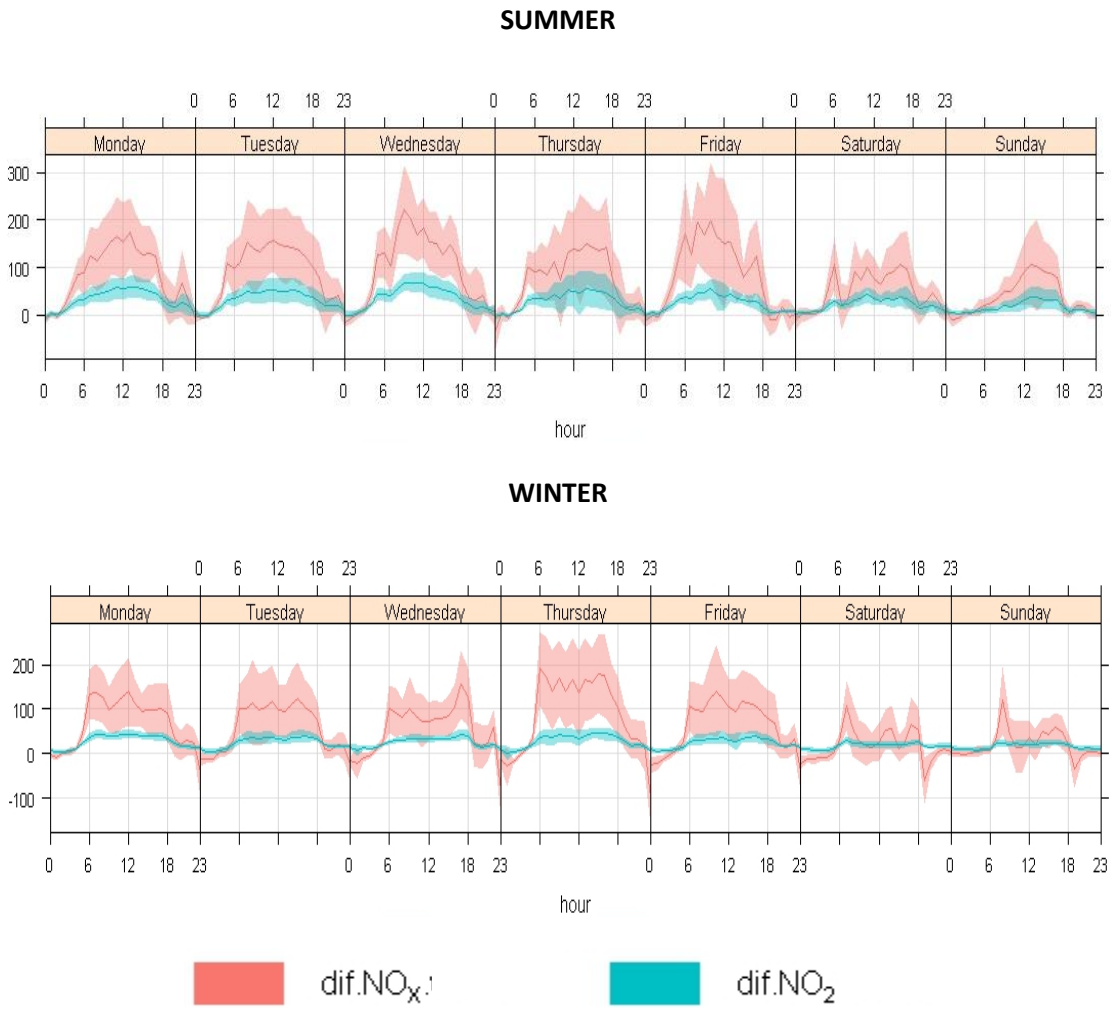


Figure 4.7: Diurnal variation profile (hourly-weekly) represents differences in concentration between indoor and outdoor $NO_X$and NO_2 during summer and winter.

Moreover, additional correlation analysis between seasons supports similar findings, with no evidence to show any correlation between the four seasons (autumn-spring- summer-winter, $p > 0.05$). The results (Table 4.4) show the strongest correlation between indoor and outdoor pollutant concentrations during winter, $R^2 = 0.97$, followed by spring and autumn; the lowest correlation value was during summer, $R^2 = 0.71$. However, the ratio value between indoor and outdoor pollutant concentrations was observed to be higher (I/O ratio = 0.30) during summer compared to other seasons.

Table 4.4: Correlation coefficient between indoor and outdoor NO_X by season.

Season	N (days)	Mean outdoor (µg m^{-3})	Mean indoor (µg m^{-3})	Indoor:outdoor ratio	I/O correlation coefficient, R^2
Spring	78	385	213	0.18	0.97
Summer	89	328	256	0.30	0.71
Autumn	82	406	395	0.18	0.86
Winter	116	455	403	0.02	0.94

4.6 Discussion of initial findings

The results showed that the distribution of indoor and outdoor pollutants in a mechanically ventilated office building located close to significant sources of pollution varied substantially and consistently with natural drivers of ventilation, particularly meteorological conditions, depending on the degree of exposure to the ambient environment.

The data analysed show the diurnal variation profile illustrated an extreme indoor concentration of NO_X and NO_2, particularly during rush hour on working-days (averaging 700 µg $m^{-3}$and 160 µg m^{-3} outdoor $NO_X$and NO_2, 500 µg $m^{-3}$and 120 µg m^{-3} indoor $NO_X$and NO_2). The concentration levels then dropped at the weekend and reached almost the same concentration. These results suggest that the majority of indoor NO_X and NO_2 can be attributed to the outdoor source. This pattern of concentration may possibly be explained by the lack of ventilation inside the building and indoor pollutant contributions from outdoor sources due to infiltration within the building envelope. On the other hand, a different diurnal variation profile was observed for indoor-outdoor airborne PM when

compared to gaseous pollutant species. High peak concentrations of PM_{10} and $PM_{2.5}$ were observed during occupied periods, with maximum ranges of 80 µg m^{-3} and 12 µg $m^{-3}$for PM_{10} and $PM_{2.5}$, respectively.

Overall, the high concentrations of indoor gaseous pollutants and airborne PM demonstrated in this study were driven by several factors, such as outdoor source penetration, meteorological conditions, street canyon effects and building occupancy. The security personnel employed in the main entrance area have experienced respiratory problems, possibly exacerbated by their personal/occupational exposure to pollutants in this area. They complain of having noticeable deposits of soot on their hair and skin, particularly the face. Various steps were undertaken by building management to overcome this problem, such as having only one entrance way, and requiring anyone entering reception to press a button to open the doors as opposed to an automatic sensor. However, the problems remain. Further, the long term monitoring characterisation in this study may indicate that the penetration within the building envelope may contribute to outdoor sources being transported indoors. Thus, further investigation has been made to determine any leakage or cracks in the building, particularly at the main entrance. The output of the visual investigation is illustrated in Figure 4.8. The gap and small hole between the automated doors possibly explain the penetration that occurred at this site, particularly at the weekend.

Due to penetration causing higher indoor pollutant sources and personal health complaints by security staff, the building manager agreed to works to improve the main door design to make them more resistant to outdoor air penetration. The automated door was upgraded between 14th and 20th March 2011, shown before and after in Figure 4.9. Moreover, a control measure campaign (before and after the doors upgrade) was undertaken to examine any changes in pollutant concentration after the door design improvements.

Figure 4.8: The small gaps between the automated doors were determined during site investigation.

Figure 4.9: The doors upgrade (before and after).

4.7 Additional study phase: Building design improvement

After one week of improvement works, both pollutants (gaseous pollutants and airborne PM) were monitored to characterise any changes due to the building design improvement, particularly for indoor pollutant concentration. A control measure in this analysis was delivered prior to these dates:

a. 25th February until 13th March 2011 - *before.*

b. 21st March until 6th June 2011 - *after.*

Pollutant characteristics are illustrated in Figures 4.10 and 4.11. Figure 4.10 shows a diurnal variation profile representing the concentration differences between indoor and outdoor NO_X and NO_2 before and after building design. Hourly mean profiles show a typical pattern of NO_X and NO_2 concentration with rapid increments during rush hour in the morning. When both of the study phases (before and after) were compared, no clear differences were observed for NO_X and NO_2 concentrations, except for those during rush hour in evening time, at 1700 hours. Nevertheless, box plot and statistical comparison (Figure 4.12) demonstrated the significant reduction ($p < 0.05$) of I/O ratio at the weekend for the concentration of pollutant species NO_X and NO_2.

In addition, a concentration difference of indoor and outdoor PM_{10} was demonstrated in a different pattern (Figure 4.11). The hourly mean concentration was recorded at a constant value before the door's upgrade, with a difference mean of -10 µg m^{-3}. Indeed, the negative value of PM_{10} concentration also shows that indoor concentration was always higher than outdoors. However, after the door's upgrade, two clear local peak concentrations were recorded during rush hour in the morning and evening time, with maximum differences of about -2.3 µg m^{-3} and -38.2 µg m^{-3}, respectively. Nevertheless, at other observation times, mean differences in concentration in were recorded higher outdoor than indoors. Further, a clear pattern of differences was illustrated in weekly profile, where positive reduction was observed after the door's upgrade throughout the measurement periods, with mean differences of concentration improving from -10 µg m^{-3} to 10 µg m^{-3}. This finding shows a clear decrease of indoor concentration after building design improvement. Furthermore, box plot and statistical comparison in Figure 4.12

support the above findings. The distribution ratio of PM_{10} a significant reduction ($p < 0.05$) for both measurement time periods, during weekdays and at the weekend.

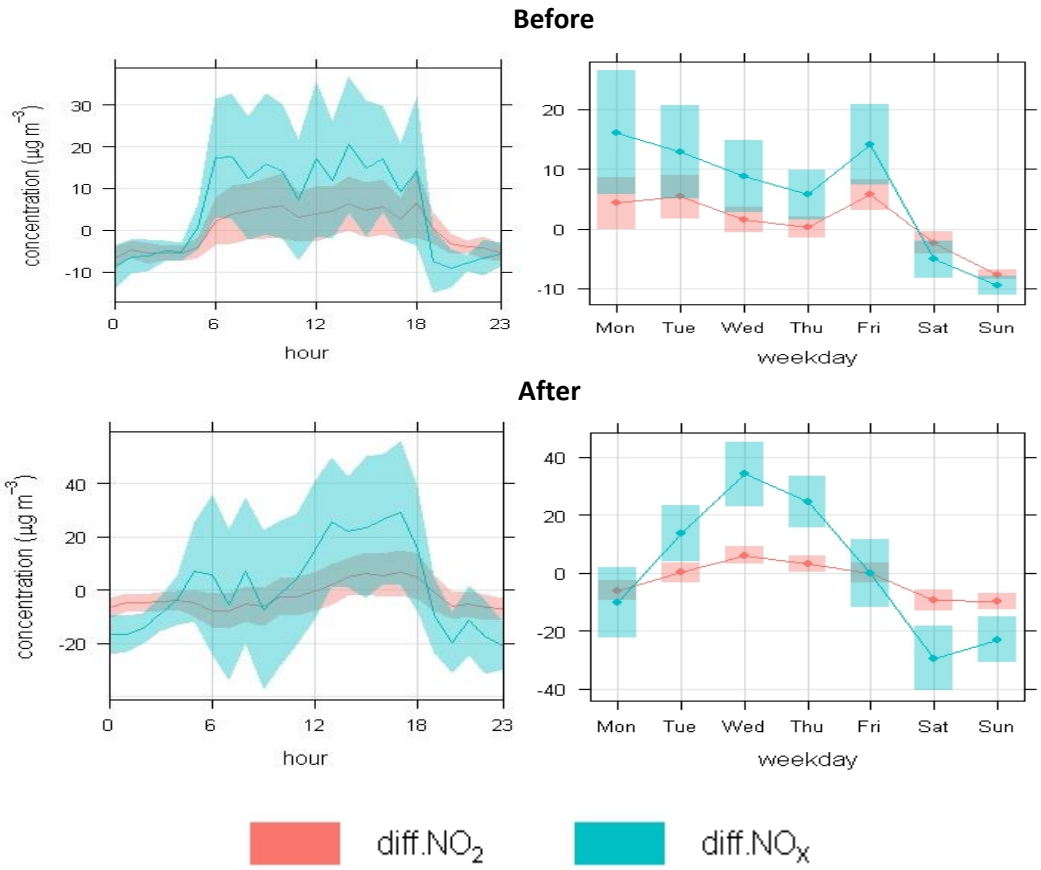


Figure 4.10: Diurnal variation profile on concentration differences between indoor and outdoor $NO_X$and NO_2 prior to building design improvements.

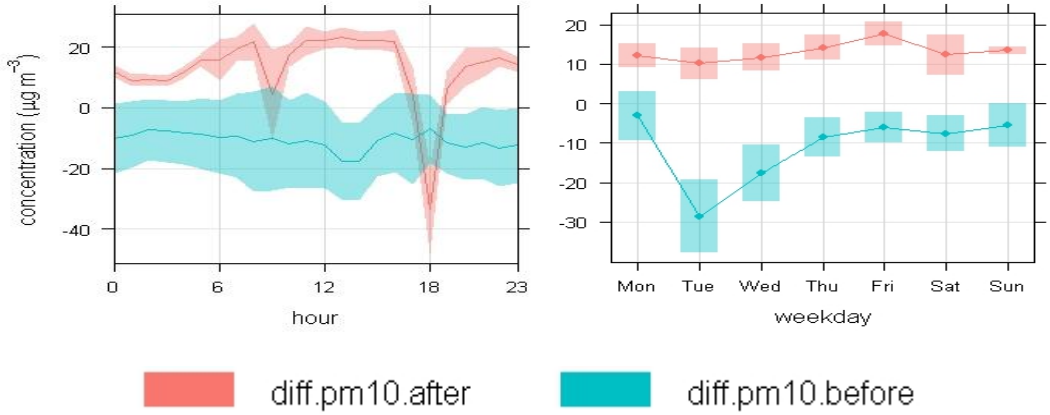


Figure 4.11: Diurnal variation profile on concentration differences between indoor and outdoor PM_{10} prior to building design improvements.

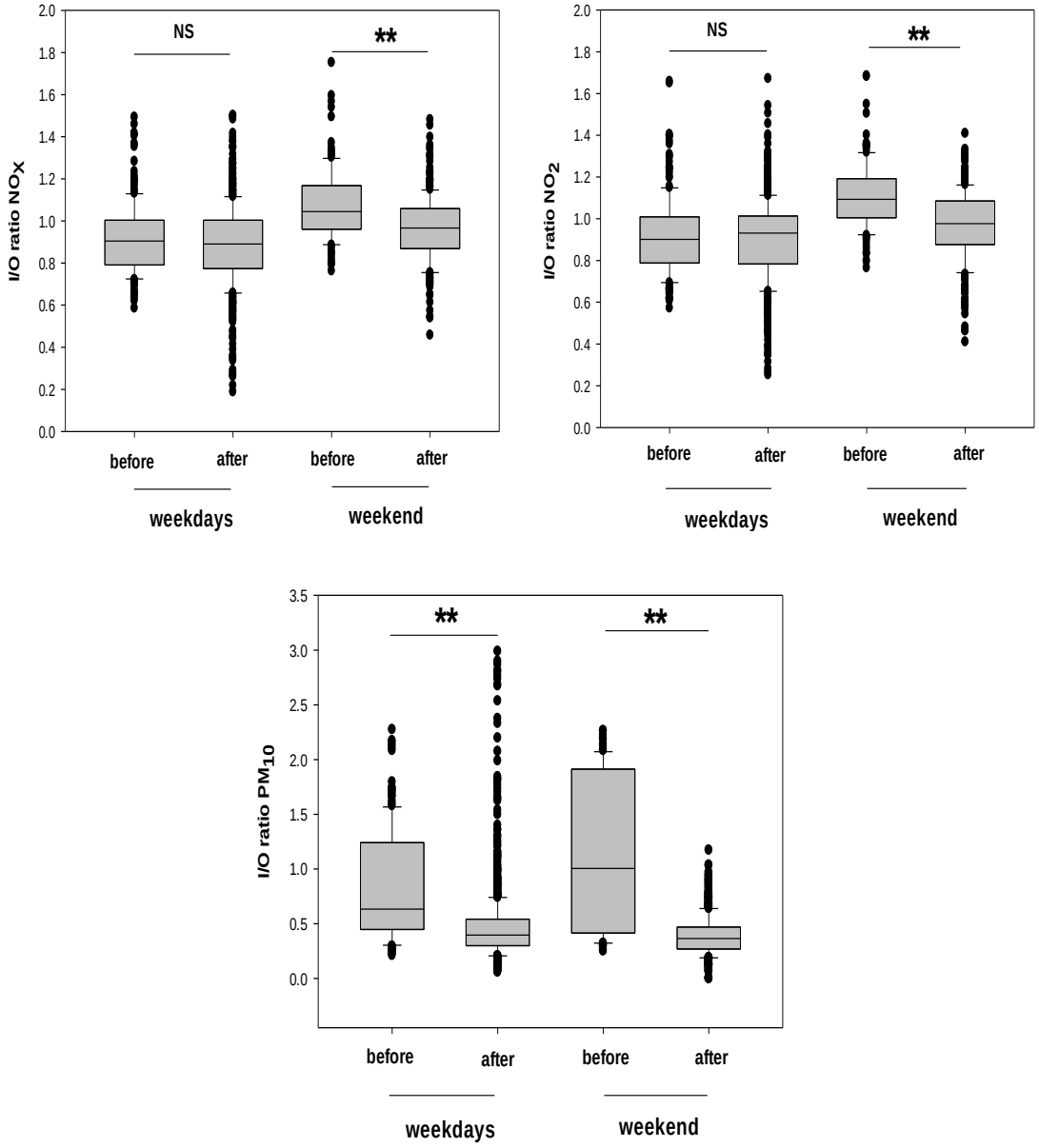


Figure 4.12: I/O ratio comparison on gaseous pollutants ($NO_X$and NO_2) and airborne PM ($PM_{10}$and $PM_{2.5}$) concentration during additional study phase (before/after doors upgrade).

*Notes:Statistical comparisons of I/O ratios (weekdays and weekend) were performed using a student t-test. Data marked with an * and ** indicate significant differences between two groups, $p < 0.05$ * and $p < 0.001$ ** respectively.*

4.7.1 Overall discussion

The aim of the work undertaken in this chapter was to better understand the nature of urban traffic-derived pollution from a range of pollutants species, and to relate these with indoor air quality and meteorologically driven factors. The long term monitoring database established in this study revealed considerable variations between indoor and outdoor pollutants in this mechanically ventilated office building.

An extreme of indoor NO_X and NO_2concentration, as illustrated in the diurnal variation profile analysis, suggests that the majority of indoor NO_X and NO_2 could be attributed to outdoor sources. This pattern of concentration may possibly be explained by a lack of ventilation inside the building, and indoor pollutants contributed from outdoor sources due to infiltration of the building envelope. Several studies support these findings, dealing with ventilation and outdoor pollutant transportation indoors due to penetration and/or infiltration, particularly in urban environments (Chen et al. 2010, Hayashi et al. 2002, Bady et al. 2008, Niachou et al. 2008). However, most of these studies were conducted with experimental models without taking into account building occupancy factors. Nevertheless, a detailed study in a real office building by Tung et al. (1999) discovered the role building fabrics, door gaps and window louvers play in reducing the amount of outdoor pollutants into the building by infiltration. In addition, Hamdy et al. (2010) revealed that the air tightness of a building had a strong impact on the penetration of outdoor gaseous pollutants into the building without absorption.

Further, Mendell et al. (1996) investigated the relationship between ventilation system types and office worker symptoms (n = 880) in California, USA during the summer of 1990. This study found that the higher adjusted prevalence of most health symptoms was correlated with both mechanical and air-conditioned ventilation relative to natural ventilation. Health symptom odd ratios were for dry or itchy skin (mechanical: odd ratio = 6.0, CI = 1.6 – 22; air-conditioned: odd ratio = 6.0, CI = 1.7 – 21) and lower respiratory symptoms (mechanical; odd ratio = 2.9, CI = 0.7 – 11; air-conditioned: odd ratio = 4.0, CI = 1.1 – 15). Overall, they concluded that health symptoms increased within mechanically ventilated and air-conditioned US buildings.

Moreover, the findings of diurnal variation profiles are supported by polar frequency plot analysis, which revealed that meteorological conditions (wind speed and direction) have significant effects on transferring pollutants indoors. Further, the majority of outdoor NO_X and NO_2 concentrations was transported indoors and most likely driven by local pollution sources due to street canyon effects. A simulation study by Bady et al. (2006) and Bady et al. (2011) had similar findings. They found that indoor pollutant concentration in an urban building with a street canyon orientation was affected by wind ventilation performance. Indeed, another recent experiment in a real building found that, rather than ventilation rate, building density and wind flow played a major role in the dilution and removal of pollutants in the urban building area (Buccolieri et al. 2010).

A different diurnal variation profile was observed for indoor-outdoor airborne PM when compared to gaseous pollutant species. High peak concentrations of PM_{10} and $PM_{2.5}$ were observed during occupied periods, with maximums of 80 µg m^{-3} and 12 µg $m^{-3}$for PM_{10} and $PM_{2.5}$, respectively. Local peak indoor PM concentration was believed to be driven by building occupancy and PM suspension, particularly for larger particles (Branis et al. 2005, Branis and Safranek 2011). In addition, ratio and correlation analyses in this study suggest that in the absence of people inside the building, the proportion of indoor PM concentration may be contributed from outdoor PM sources, particularly at the weekend. A number of studies show a significant correlation of PM suspension due to building occupancy (Chao et al. 1998, Branis et al. 2005, Hovorka et al. 2005, Fromme et al. 2007). Even though many of these studies were examined in school environments, nevertheless, the theory of PM suspension and deposition in all microenvironments would be homogenous in most cases.

To date, only one recent study has been done to characterise ultrafine particles inside and outside commercial buildings in long term regimes. Wang et al. (2010) revealed that I/O ratios generally increase with particle size. They also found that I/O ratios in the summer were higher than those in the winter. However, air exchange rate and building occupancy may influence the correlation between indoor-outdoor ultrafine particle number concentrations. In addition, Kudo and colleagues (2011) demonstrated in their study that

a high-rise building showed that ultrafine particles of elemental carbon from vehicle exhaust can reach the upper atmosphere regardless of season. They believed this phenomenon was due to the high sensitivity of ultrafine particles in the atmosphere, which diffused uniformly along the street canyon both vertically and horizontally.

In an additional study phase, building design improvements demonstrated air tightness, and gave building envelopes good protection from external sources (Poupard et al. 2005, Alshitawi et al. 2009, Alshitawi & Awbi 2011). The existence of indoor pollutant concentrations during unoccupied periods with a lack of ventilation (when it was switched off), may explain the importance of proper ventilation for dilution and removal of pollutants inside a building (Lu et al. 2007). A study by Ni Riain et al. (2003) also suggested that penetration factors cannot rely on pollutant concentrations, but must relate to other natural factors such as temperature differences inside and outside a building.

4.8 Conclusion

The new results in this study possibly illustrate the typical scenario at most mechanically ventilated office buildings in London adjacent to a busy road. However, the fluctuation of indoor-outdoor pollutant concentration within building envelopes were also driven by other factors such as urban building orientation, the complexity of building occupancy and different set of energy use. In addition, the fact that the door upgrade did not solve the high NO_2 problem (as shown in the control measure study) shows that even small breaks in the building envelopes can allow ingress of large volumes of outdoor pollution.Thus, this finding highlights the importance of building design on indoor microenvironments, particularly for offices adjacent to a busy road.

Chapter V

Characteristics of indoor-outdoor particulate oxidative activity in two contrasting buildings in London

5.1 Introduction

In recent years, there has been an increased interest in IAQ, with a focus on sources, concentration levels and human exposure to airborne PM. Epidemiological studies have consistently demonstrated that ambient PM has profound negative health impacts, resulting in increased short-term daily mortality and hospital admissions (Katsouyanni et al. 2001, Katsouyanni 2003). Airborne PM from the ambient environment, including vehicle combustion and industry, may potentially increase indoor pollutant concentration via infiltration, as well as being released indoors. Further, previous studies have shown a strong relationship between indoor PM and asthmatic exacerbation, particularly amongst fragile groups such as children, pregnant women and the elderly (Firdaus & Ahmad 2011, Hunt et al. 2011, Jie et al. 2011). However, the variation in PM dose concentration related to the indoor-outdoor concentration alone cannot determine the health risks of exposure. Particulate-induced oxidative stress has been proposed as having a key role to examine health effects, particularly in humans (Boogard et al. 2011).

Several studies have shown that ambient PM has a strong impact on antioxidant scavengers in the human RTLF defence system. Antioxidant components such as ascorbate were depleted in a PM dose dependent pattern (Zielinski et al. 1999, Mudway et al. 2004, Kunzli et al. 2006), and antioxidant losses were inhibited by the presence of metal chelators(Mudway et al. 2005, Godri et al. 2011). Furthermore, a field study to quantify the contribution of waste transfer station activity in London demonstrated the increment of PM oxidative potential and elevation of trace metal arising from such activity (Godri et al. 2010a, Godri et al. 2010b).

However, to the best of my knowledge, no previous study has investigated indoor particulate-induced antioxidant depletion in human RTLF. Therefore, utilising this approach there is an opportunity to better understand PM characteristics and the relationship of indoor and outdoor particulate oxidative toxicity.

5.1.1 Research aims and justification

PM oxidative activity was examined by quantifying its capacity to deplete antioxidants from the synthetic RTLF model. As described in Chapter II, section 2.6, PM_{TSP} (Total suspended particle) samples were collected from both study sites; airborne PM OP analysis was undertaken at the Lung Biology Group, King's College London by using a defined PM OP assessment (Duggan et al. 2004). The long-term PM OP dataset was also considered in respect of the influence of the respective building characterisation and occupant diaries, which were also established in this study. Such a unique dataset should enable greater understanding of the variability and drivers of particle toxicity and, ultimately perhaps, help to establish a closer association between health effects and particulate emissions.

In addition, this chapter demonstrated oxidative activity in the context of PM $OP^{antioxidants}$ metrics, which was shown to have more relevance than particulate mass; which if measured alone would obscure any change in source in the transfer of pollutants into a building. Two metrics of PM oxidative activity were determined dependent on the approach taken: ascorbate (OP^{AA}) andglutathione (OP^{GSH}), which provide a measure of the toxicity of the indoor-outdoor PM over the filter's exposure period.

This study aims to establish spatial and temporal descriptive analysis of the indoor-outdoor PM OP dataset. The relationship between ascorbate (OP^{AA}), glutathione (OP^{GSH}) and gaseous pollutants, as well as seasonal variation, are used to create a basic characterisation of the metrics. Specifically, the main objectives of this chapter are divided according to the study sites as follows:

Naturally ventilated school building (urban background site)

a. The differences in PM-induced oxidative activity between indoors and outdoors,according to the building characteristics.
b. The differences in PM OP relation to the metrics in building occupancy/classroom activity.
c. The differences in indoor-outdoor PM OP metricsaccording to seasonal variation.

Mechanically ventilated office building (roadside site)

a. The differences in PM-induced oxidative activity between indoors and outdoors, according to building characteristics.
b. The differences in PM OP metrics prior to main door improvements.

5.1.2 Methods

The collection, extraction, resuspension and RTLF exposure of indoor and outdoor particle filters were discussed in Chapter II, section 2.7, Osiris TSP filters were collected from March 2010 until May 2011 from both study sites, which were classified as roadside and urban background sites. As mentioned in Chapter II, section 2.2.2, due to the difficulty of installing Osiris monitors at the roadside, the distribution of collected filters from these sites was not even. Details of the actual filters collected will be explained in the results section of this chapter.

The PM OP dataset is represented using per unit mass (OP μg^{-1}) and per unit volume (OP m^{-3}) metrics. When presented as per unit mass, the measure represents the oxidative activity of each microgram of PM, independent of the indoor-outdoor particle loading. These datasets were then converted to OP per unit volume by multiplying by the mean mass measurement of PM_{TSP} in $\mu g\ m^{-3}$ over the filter's exposure period.

The mean distributions of indoor-outdoor PM OP parameters were demonstrated as a box plot analysis, and the data were plotted and displayed graphically using GraphPad Prism 5 and SigmaPlot 12.0. Also, a Spearman's rank correlation grid was produced to show the relationship between weekly and biweekly mean background OP^{AA} and OP^{GSH} per

unit mass and per unit volume, and also to show the pollutants as well as explanatory variables owing to seasonal variation.

5.2 Results

5.2.1 Filter collection and filter exposure periods

The filter exposure and collection procedure were discussed in Chapter II, section 2.6. All filter papers were processed and stored at $4^{o}C$ in the weighing room Bexley Sidcup facility. A day before each batch of PM filters were extracted filters were transferred into $-10^{o}C$ chest freezer in the Lung Biology laboratory at King's College London. These procedures were undertaken as quickly as possible and at $4^{o}C$ in order to prevent any loss of volatile and semi volatile species on PM filters. In addition, to avoid inconsistency on PM mass pre and post extraction measurement accuracy, all exposed filter papers were conditioned and weighted under similar conditions in consistent temperature and humidity.

The filter collection and their absolute PM masses from each study site (naturally ventilated school building and mechanically ventilated office building) are shown inTable 5.1 and 5.2 respectively. In this Table filters have relevant building diary activity and occupancy information. Due to the variety of classroom activities within each 2-week exposure period, the dominant classroom activity was selected based on the teacher's records. Furthermore, it is worth noting that there are two PM mass values. The first is the absolute PM mass obtained from the OSIRIS monitor mean measurement according to filter exposure periods. The second is the extracted PM mass which was measured as pre and post PM extraction procedure and is reported in appendix C.

In order to check for remaining particles on the filter after the extraction procedure, re-extraction experiments were undertaken for each sample filter, as described in Appendix C. Each of the samples filters from the re-extraction experiment shows less than 20% antioxidants depletion rate when compared to the first extraction. Furthermore, in the interest of learning more about the filter material, the Osiris sample filters were also tested and compare to other types of filters from similar location, such as TEOM filter. The results shows almost similar depletion rate with MFG OSIRIS filters. However, the

TEOM filter oxidative activity from urban background was far higher than MFG OSIRIS filters (in terms of per µg – PM mass collection). These findings may suggest that TEOM filter had longer exposure time, and also driven by cofounder biased –loss of semi-volatile organic compound during filter handling. Based on these findings, I concluded that the first extraction procedure to produce PM OP dataset in this study was considered reliable and representative.

Naturally ventilated school building

A total of 50 PM_{TSP} filters were collected throughout the 1 year monitoring campaign (March 2010 – March 2011) at this site, representing the indoor and outdoor PM filter environments. The differences between indoor and outdoor TSP mass ratio were recorded according to different types of building occupancy and classroom activity (Table 5.1). The highest collection rate was obtained while classrooms were occupied, especially during winter time.With the window closed, the average mass ratio was 2.96 (SD ± 1.34);the mass ratio during summer time was 1.74 (SD ± 0.70),when the window was frequently open.

Mechanically ventilated office building

A total of 7 OSIRIS PM_{TSP} filters and 7 TEOM PM_{10} filters were collected every week throughout the 3 month monitoring campaign (March until May 2011) to compare oxidative activity from both filter types (Table 5.2). Mean TSP mass collected from inside the building was 1.15 (SD ± 0.61), and 2.05 (SD ± 0.62) from outside building (the TEOM analyser was located about 500 metres from the building). The ratio of TSP mass at this site waslower 0.53 (SD ± 0.16) than the urban background site, due to high PM exposure from heavy traffic on the nearby road.

Table 5.1: Date of filter collection and PM mass obtained according to building characteristics from naturally ventilated school building.

Filter No	Sampling	Exposure Period	Building occupancy & No of occupants *	Classroom activity **	Absolute Mass (mg)	Indoor/Outdoor mass ratio
Os 1	Indoor	9-16 Mar	Occupied	Paper painting	0.91	4.14
Os 2	Outdoor	*(1 week)*	25	Soil & Insects	0.22	
Os 3	Indoor	17-24 Mar	Occupied	Paper painting	0.63	3.00
Os 4	Outdoor	*(1 week)*	24	Quiz	0.21	
Os 5	Indoor	24-30 Mar	Occupied	Briefing	0.47	1.09
Os 6	Outdoor	*(1 week)*	15	Outdoor	0.43	
Os 7	Indoor	30 Mar-6 Apr	Partially occupied		0.33	1.65
Os 8	Outdoor	*(2 weeks)*	4		0.20	
Os 9	Indoor	7-20 Apr	Partially occupied		0.85	1.16
Os 10	Outdoor	*(2 weeks)*	4		0.73	
Os 11	Indoor	20 Apr-4 May	Occupied	Briefing	0.64	1.36
Os 12	Outdoor	*(2 weeks)*	21	Outdoor	0.47	
Os 13	Indoor	4-19 May	Occupied	Briefing	1.28	1.47
Os 14	Outdoor	*(2 weeks)*	23	Outdoor	0.87	
Os 15	Indoor	19 May-1 June	Occupied	Briefing	1.72	1.23
Os 16	Outdoor	*(2 weeks)*	22	Outdoor	1.39	
Os 17	Indoor	1 June-14 June	Partially occupied		1.91	0.62
Os 18	Outdoor	*(2 weeks)*	4		1.45	
Os 19	Indoor	14 June-29 June	Occupied	Paper painting	2.35	2.50
Os 20	Outdoor	*(2 weeks)*	33	Outdoor	0.94	
Os 21	Indoor	29 June-15 July	Occupied	Soil & Insects	1.35	2.11
Os 22	Outdoor	*(2 weeks)*	21	Outdoor	0.50	
Os 23	Indoor	15-27 July	Partially occupied		0.61	1.83
Os 24	Outdoor	*(2 weeks)*	4		0.50	
Os 25	Indoor	27 Jul- 10 Aug	School Holiday		0.62	1.66
Os 26	Outdoor	*(2 weeks)*			0.50	
Os 27	Indoor	10 Aug-26 Aug	School Holiday		0.65	1.52
Os 28	Outdoor	*(2 weeks)*			0.50	
Os 29	Indoor	2 Sept-19 Oct	Occupied	Soil	1.20	1.11
Os 30	Outdoor	*(2 weeks)*	22	Outdoor	1.08	
Os 31	Indoor	20 Oct -3 Nov	Occupied	Soil & Insects	0.58	1.26
Os 32	Outdoor	*(2 weeks)*	23	Outdoor	0.46	
Os 33	Indoor	4- 15 Nov	Occupied	Paper painting	0.67	1.76
Os 34	Outdoor	*(2 weeks)*	33	Quiz	0.38	
Os 35	Indoor	16 Nov-7 Dec	Occupied	Soil & Insects	0.67	1.76
Os 36	Outdoor	*(2 weeks)*	31	Paper painting	0.38	
Os 37	Indoor	8-21 Dec	School Holiday		0.87	1.77
Os 38	Outdoor	*(3 weeks)*			0.49	

Filter No	Sampling	Exposure Period	Building occupancy & No of occupants *	Classroom activity **	Absolute Mass (mg)	Indoor/Outdoor mass ratio
Os 39	Indoor	*22 Dec – 12 Jan (2 weeks)*	School Holiday		0.49	1.40
Os 40	Outdoor				0.35	
Os 41	Indoor	13-27 Jan *(2 weeks)*	Partially occupied 4		0.53	0.77
Os 42	Outdoor				0.69	
Os 43	Indoor	28 Jan- 8 Feb *(2 weeks)*	Snow		0.92	1.74
Os 44	Outdoor				0.53	
Os 45	Indoor	9-23 Feb *(2 weeks)*	Occupied 11	Paper painting Briefing	1.79	3.38
Os 46	Outdoor				0.53	
Os 47	Indoor	24 Feb- 9 Mar *(2 weeks)*	Partially occupied 8	Visitor	1.40	1.52
Os 48	Outdoor				0.92	
Os 49	Indoor	10- 24 Mar *(2 weeks)*	Occupied 15	Paper painting Outdoor	1.90	4.13
Os 50	Outdoor				0.46	

Sampling period and building occupancy/characteristics for each collection filter are listed.

*Note: Building occupancy * occupied: classroom has been used by students/teachers; partially occupied: teacher-on-duty & classroom has been used intermittently; school holiday: site closure. Classroom activity **: dominant classroom activity during week based on teacher's teaching records.*

Table 5.2: Collection dates and PM mass obtained according to building characteristics from mechanically ventilated office building (roadside).

Filter No	Sampling	Exposure Period	Building occupancy *	Building characteristics **	Absolute Mass (mg)	Indoor/Outdoor mass ratio
Os 1	Indoor	17-24 Feb *(1 week)*	Yes	before	1.79	0.50
TEOM 1	Outdoor				2.32	
Os 2	Indoor	24 Feb-7 Mar *(1 week)*	Yes	before	2.11	0.65
TEOM 2	Outdoor				3.21	
Os 3	Indoor	7-16 Mar *(1 week)*	Yes	before	0.44	0.33
TEOM 3	Outdoor				1.63	
Os 4	Indoor	17-28 Mar *(1 week)*	Yes	after	0.85	0.52
TEOM 4	Outdoor				1.65	
Os 5	Indoor	28 Mar- 4 Apr *(1 week)*	Yes	after	0.98	0.49
TEOM 5	Outdoor				1.98	
Os 6	Indoor	5-12 Apr *(1 week)*	Yes	after	1.21	0.55
TEOM 6	Outdoor				2.21	
Os 7	Indoor	13-20 Apr *(1 week)*	Yes	after	0.64	0.48
TEOM 7	Outdoor				1.32	

Sampling period and building occupancy/characteristics for each collection filter are listed.

*Note: Building characteristics ** before/after: before & after doors upgraded.*

5.2.2 The characterisation of indoor-outdoor PM OP at naturally ventilated school building – urban background

Generally, a broad range of oxidative activity was present between indoor and outdoor PM when compared on an equal mass basis (50µg/ml). PM $_{TSP}$ samples from both study sites showed significant losses of antioxidants in the RTLF over the 4 hour incubation, $p < 0.05$. The raw PM OP dataset is illustrated in Figures 5.1 – 5.4.

With respect to the OP^{AA} ug^{-1}, as shown in Figure 5.1, the highest depletion rate was observed between 15th December 2010 and 17th February 2011, mean OP^{AA} ug^{-1} 0.68 ± 0.02, whereas the lowest depletion rate was between 14th June and 29th June 2010, mean 0.21 ± 0.02. Further, as shown in Figure 5.2, the OP^{AA} m^{-3} appears to have had a lower depletion rate, from 19th June until 8th November 2010, mean 10.32 ± 1.22. However, the highest depletion rate was observed at the beginning and at the end of the monitoring study campaign. The results revealed that indoor PM_{TSP} samples had higher depletion rates than outdoors within those periods; mean was 38.85 ± 6.22 indoors and 18.65 ± 7.84 outdoors.

In contrast, the OP^{GSH} ug^{-1} and OP^{GSH} m^{-3} wasobservedvaries between indoor-outdoor PM samples (Figure 5.3 and 5.4). The highest OP^{GSH} m^{-3} wasrecorded during the first sampling periods (24th March – 30th March 2010), mean 31.2 ± 9.5. It worth noting that the increment of indoor PM OP during these periods was due to a high indoor concentration derived from cleaning activity inside the classroom. The cleaning activity was carried out in order to check the indoor PM monitor sensitivity to indoor local dust. Interestingly, the mean value of OP^{GSH} m^{-3} decreased rapidly in the following week after cleaning works. In addition, OP^{GSH} m^{-3} was observed to be lowest during the Easter break, between 8th and 20th April 2010, however, overall no clear trend is apparent throughout the sampling periods. The lowest depletion rate was observed during the Easter term break, which was from indoor PM samples, mean 0.11 ± 0.02. The highest OP^{GSH}µ$g^{-1}$was observed between 25th October and 8th November 2010, mean 0.51 ± 0.12 indoors.

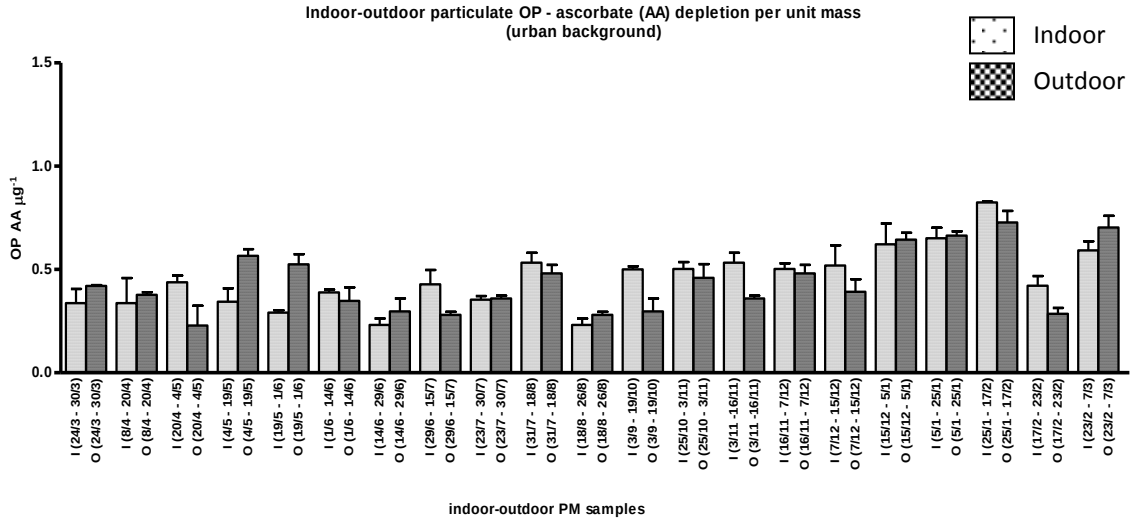


Figure 5.1: Oxidative particulate OP metric: AA depletion per unit mass between indoor and outdoor PM $_{TSP}$ from naturally ventilated school building (urban background).

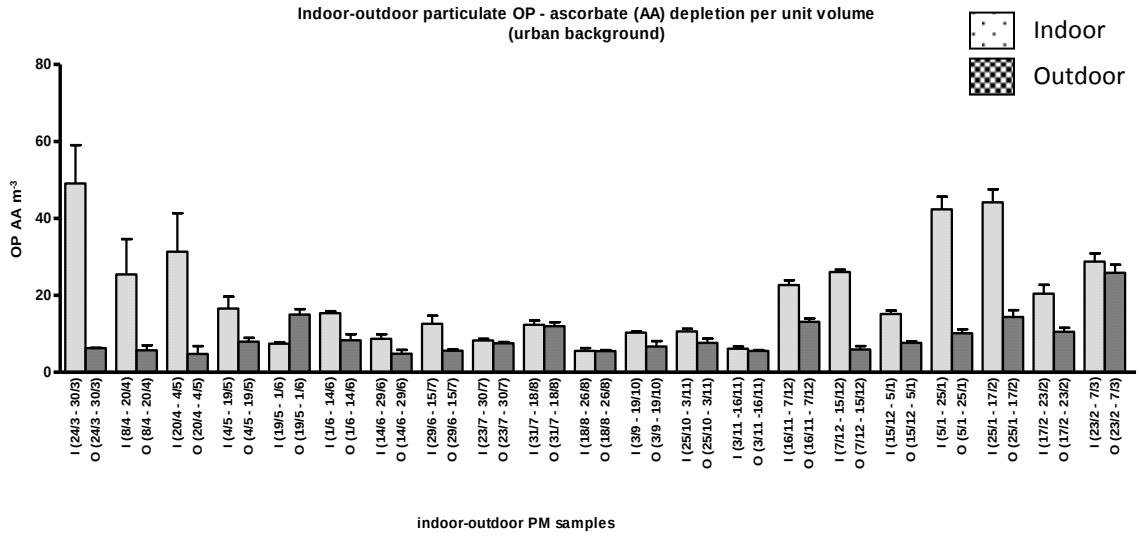


Figure 5.2: Oxidative particulate OP metric: AA depletion per unit volume between indoor and outdoor PM $_{TSP}$ from naturally ventilated school building (urban background).

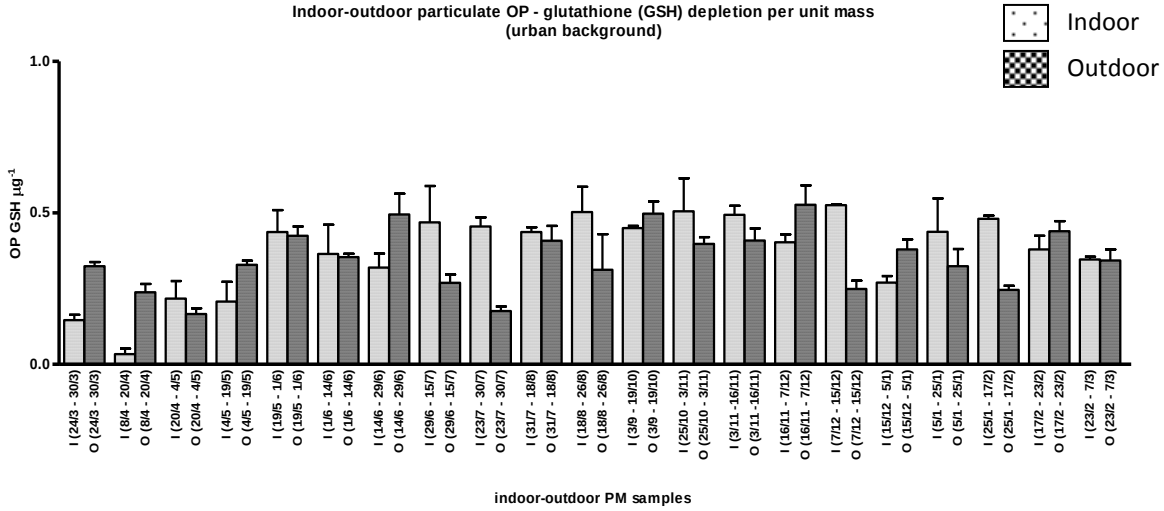


Figure 5.3: Oxidative particulate OP metric: GSH depletion per unit mass between indoor and outdoor PM $_{TSP}$ from naturally ventilated school building (urban background).

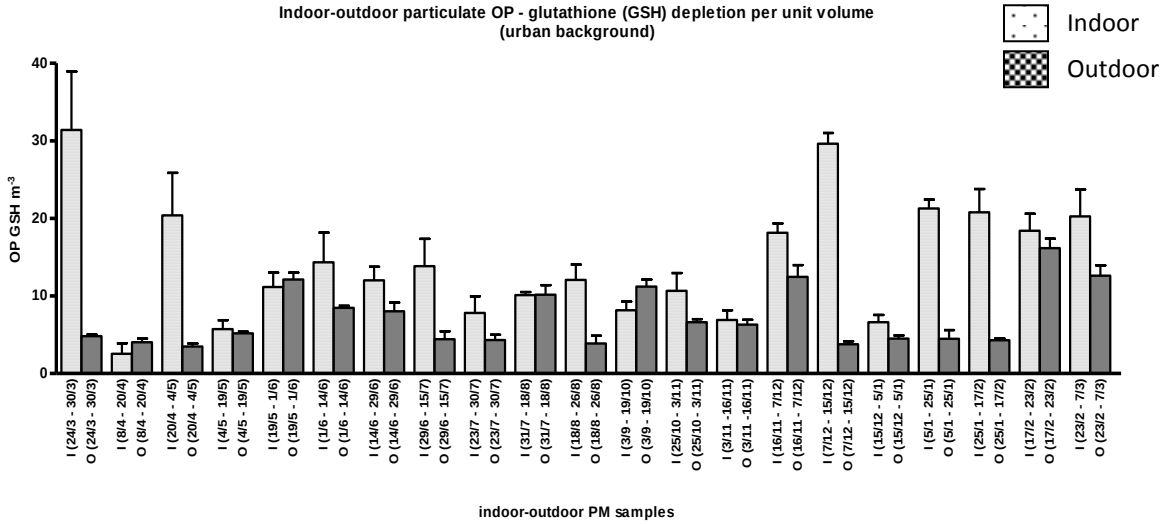


Figure 5.4: Oxidative particulate OP metric: GSH depletion per unit volume between indoor and outdoor PM $_{TSP}$ from naturally ventilated school building (urban background).

Overall, when indoor-outdoor PM OP averages were compared (Figure 5.5), OP $^{antioxidants}\mu g^{-1}$ (including AA and GSH) did not show any significant differences between indoor and outdoor PM samples. However, OP ^{antioxidants} m^{-3} showed a significant difference between indoor and outdoor PM samples with $p < 0.05$. There is a clear pattern in this analysis whereby the indoor PM samples had higher depletion rates in the volume concentration compared to outdoors. This finding may indicate that indoor concentration was driven by building occupancy. The majority of the high peak indoor PMconcentrations in the classroom were observed while classrooms were occupied.

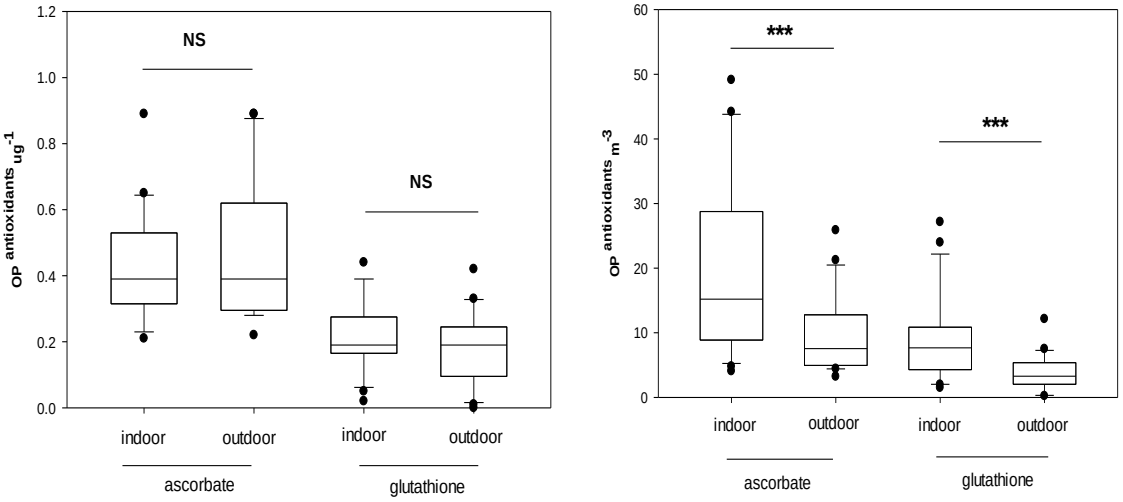


Figure 5.5: Oxidative particulate OP metric: AA and GSH depletion per unit mass and volume between indoor and outdoor PM TSP at naturally ventilated school building (urban background).

*Note: Note:Statistical comparisons of each mean particulate OP metric were performed using a one way ANOVA with post hoc analysis performed using unpaired t-test.Where data has shown significant differences between indoor-outdoor PM samples for both OP antioxidant activity, *** is significant p-value less than 0.001 (indoor-outdoor OP^{AA} m^{-3} = 0.005, indoor-outdoor OP^{GSH} m^{-3} = 0.004).*

The relationship between indoor and outdoor PM- induced AA & GSH losses

In order to investigate the OP metric relationship between indoor and outdoor PM samples further, the correlation factor was determined between these two OP metrics. Table 5.3 clearly shows a significant correlation in OP^{AA} ug^{-1}, which may indicate that similar sources make up a large proportion of outdoor reactive PM into indoors. However, there is no clear evidence of a relationship between indoor and outdoor PM OP in other parameters.

Table 5.3: Spearman's correlation between indoor and outdoor OP^{AA} and OP^{GSH} (μg^{-1} and m^{-3}).

	Indoor OP^{AA} ug^{-1}	Indoor OP^{AA} m^{-3}	Indoor OP^{GSH} ug^{-1}	Indoor OP^{GSH} m^{-3}
Outdoor OP^{AA} ug^{-1}	0.522 *			
Outdoor OP^{AA} m^{-3}		0.155		
Outdoor OP^{GSH} ug^{-1}			-0.122	
Outdoor OP^{GSH} m^{-3}				-0.047

*Note: Data are represented as means ± SD (n=3). * is significant p-value less than 0.05.*

By expanding the analysis to investigate the relationship between PM-induced antioxidants AA and GSH, the strength of this underlying association was improved when both antioxidant depletions were combined (R^2=0.80, p=0.005) (Figure 5.6). This indicates that a common component was driving the loss of these two antioxidants.

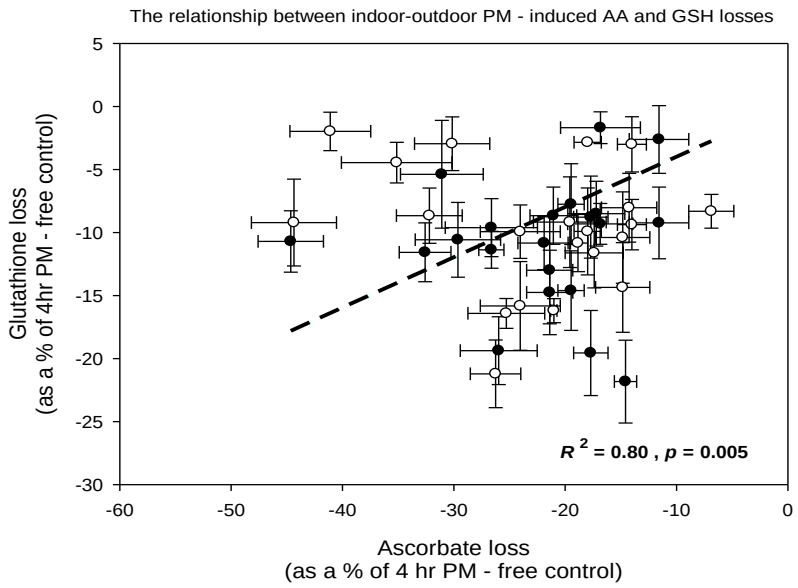


Figure 5.6: The relationship between PM-induced AA and GSH losses indoors and outdoors from naturally ventilated school building (urban background).Data presented is the correlation between the % loss of AA and GSH indoors and outdoors from TSP PM, relative to the particle free control at 4 hours. Data are represented as means ± SD (n=3). Details of the regression are inset.

The differences of PM OP metrics in building occupancy/classroom activity

In order to ascertain the influence of the presence and absence of people in the classroom on indoor and outdoor PM OP metrics, the data obtained during the one-year study campaigns were divided into two separate periods in line with the filter collection sampling periods:

a. Occupied period (classroom activity and number of occupants is recorded as described in Table 5.1).
b. Unoccupied period (partially occupied/ school holiday / term break)

It is worth noting that the weekend period was not included in this PM OP comparison, due to the minimum mass collection required for mass PM OP analysis. School holiday period observations were used to represent weekend periods, since they share a similar

absence of people and classroom activity.Additionally, the influence of building occupancy/classroom activity in indoor PM OP is compared to outdoor environments in order to investigate the contribution of active PM composition from ambient environments via building penetration.

The raw indoor and outdoor PM OP metric dataset is illustrated in Figure 5.7. The results shows $OP^{AA}\mu g^{-1}$and OP^{GSH} μg^{-1}during occupied periods were found to be significantly higher than outdoors, $p < 0.01$, mean 0.57 ± 0.18 and 0.41 ± 0.11 respectively, $p < 0.01$. However, no clear differences were found between indoor and outdoor PM $OP^{antioxidants}$ metrics during unoccupied periods. These findings offer clear evidence that a PM-driven oxidative reactant was influenced by building occupancy, particularly related to classroom activity which might plays as major contribution of total mass reactive PM composition to attribute higher antioxidant depletion. However, this observation does not only rely on an indoor contribution, but may include contribution from the outdoor environment due to pollutant penetration inside the classroom. Furthermore, PM OP ^{antioxidants} m^{-3} has shown similar findings when PM $_{TSP}$ concentrations were compared; mean indoor PM OP was 28.2 ± 5.3 for ascorbate and 20.1 ± 2.9 for glutathione. A similar homogenous pattern of OP ^{antioxidants} m^{-3} existed between both sources, however, indoor OP^{GSH} m^{-3} was found to be higher significantly during unoccupied periods, $p < 0.05$.

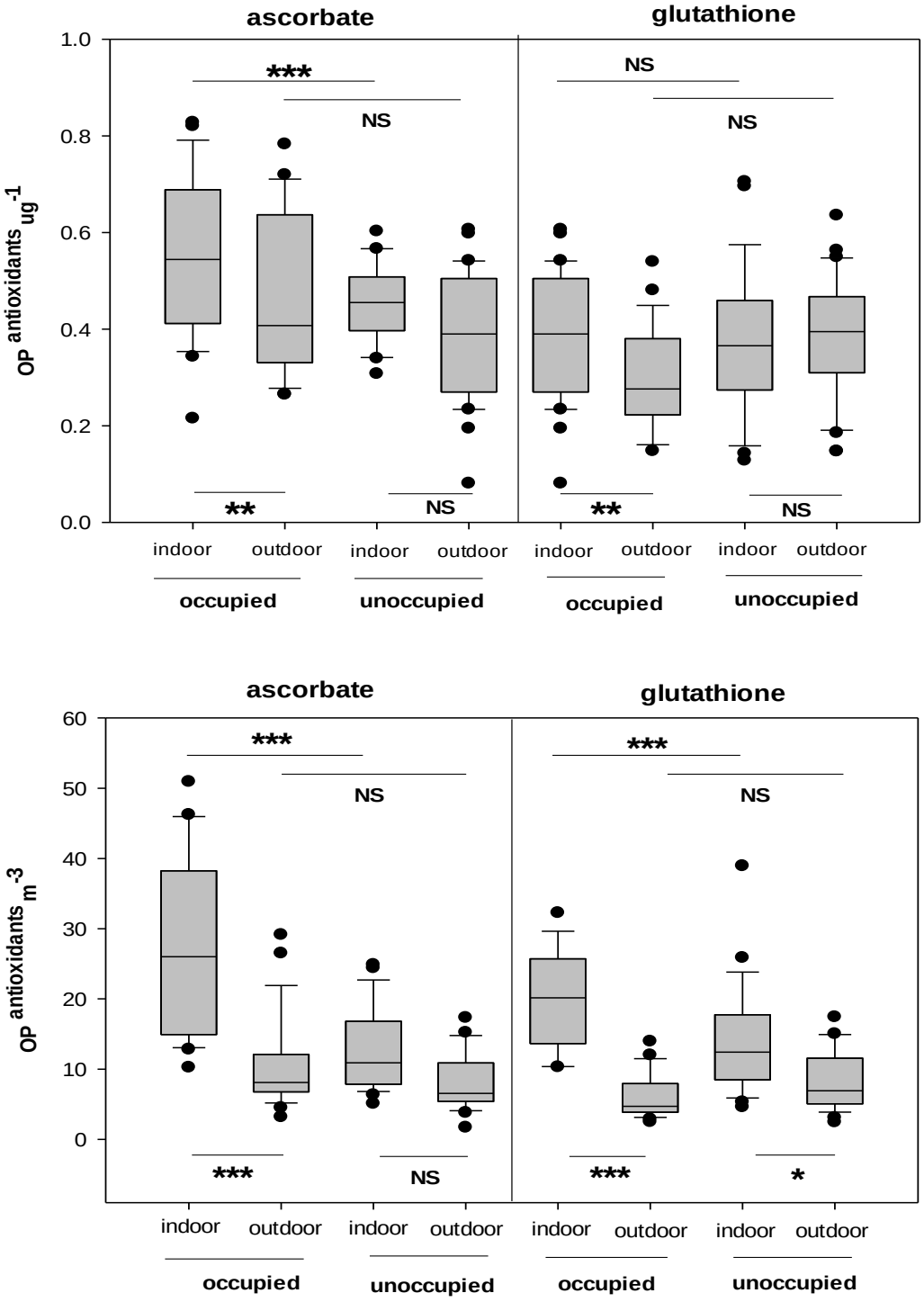


Figure 5.7: Particulate OP metric variation (OP antioxidants μg^{-1}& m^{-3}) according to building occupancy of TSP PM from naturally ventilated school building (urban background).
Notes:Statistical comparisons of each mean particulate OP metric were performed using a one way ANOVA with post hoc analysis performed using unpaired t-test.

To further examine the PM-driven oxidative activity occurring inside the classroom, PM OP metrics between occupied and unoccupied periods were also compared. The indoor PM OP ^{antioxidants} metric was found to be higher during occupied periods compared to unoccupied periods. However, no clear evidence to show significant differences in OP^{GSH} μg^{-1} between occupied and unoccupied periods was observed.

The differences between indoor and outdoor PM OP according to seasonal variation

The variability of OP antioxidant activity was next tested by looking at meteorologicallydriven factors using seasonal comparison. Two seasons were compared in this analysis: summer and winter. It is worth noting that PM OP metrics during unoccupied periods were excluded in this analysis, in order to correlate the significance of PM OP driven by building occupancy between these two seasons.

The raw datasets of indoor and outdoor PM OP metrics according to seasonal variation are shown in Figure 5.8. Generally, a homogenous pattern was observed between indoor and outdoor OP^{AA} μg^{-1} during summer and winter seasons; there is no clear evidence to show any significant difference between those PM OP metrics, $p > 0.05$. Nevertheless, indoor and outdoor OP^{AA} μg^{-1} was found to be significantly higher during the winter season when compared to the summer season. Consequently, indoor OP^{GSH} μg^{-1} was found to be higher than outdoors for both seasons; mean indoors was 0.45 ± 0.11 during summer and 0.39 ± 0.12 during winter. Further, as expected, PM OP ^{antioxidants} m^{-3} was observed higher indoors when compared to outdoors, particularly during the winter season. These findings agree with previous results on diurnal variation profiles in Chapter III, section 3.2, which indicate that the PM concentration was found to be higher during the winter season when compared to other seasons.

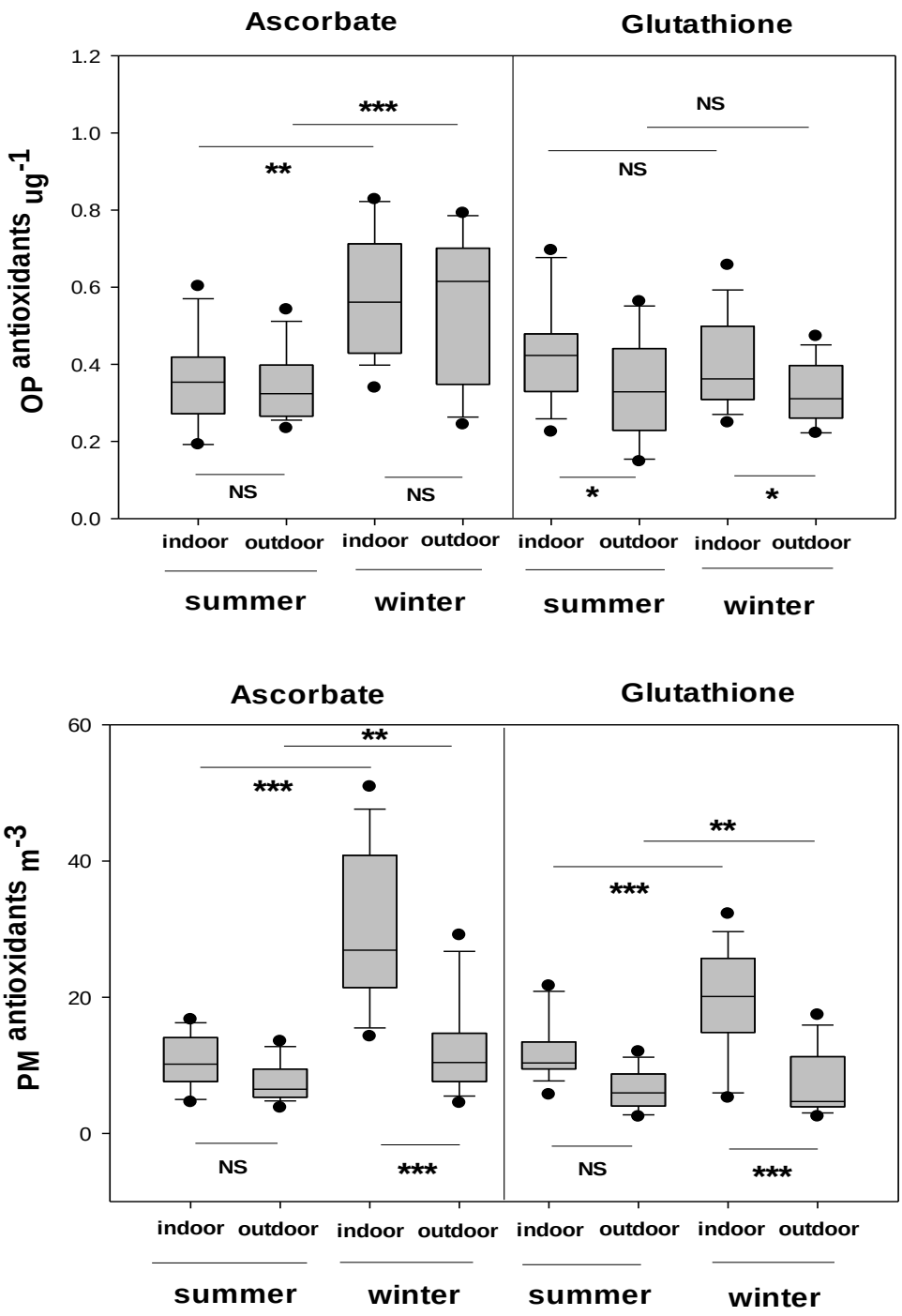


Figure 5.8: Seasonal variation (summer vs. winter) in the particulate OP metric (per unit mass and volume) of indoor-outdoor TSP PM from naturally ventilated school building (urban background).

Notes: Statistical comparisons of the AA and GSH were performed using a one way ANOVA, with post hoc analysis performed using unpaired t-test.

Overall OP^{AA} μg^{-1}metric between seasons differed significantly, but not the OP^{GSH} metric. Indoor OP^{AA} μg^{-1} during winter was significantly higher compared to summer. The winter mean depletion rate for ascorbate OP $\mu g^{-1}$was 0.56 ± 0.11 and glutathione was 0.35 ± 0.01, however for mean depletion rate during summer, OP^{AA} μg^{-1} was 0.31 ± 0.09 and OP^{GSH} was 0.39 ± 0.12. Further, indoor PM OP ^{antioxidants} m^{-3} was observed to be higher in winter, which is consistent with previous findings. Indoor winter OP^{AA} m^{-3} was 24.3 ± 5.9 and OP^{GSH} m^{-3} was 19.8 ± 2.9 and indoor summer was 14.2 ± 2.1 and 15.2 ± 1.9 for OP^{AA} and OP^{GSH}, respectively.

5.2.3 The characterisation of indoor-outdoor PM OP at mechanically ventilated office building (roadside site)

As illustrated in the raw datasets in Appendix C.3, PM $_{TSP}$ Osiris and PM_{10} TEOM samples showed significant ($p < 0.05$) losses of antioxidants in the RTLF over the 4 hour incubation period. The conversion of PM mass into PM OP metrics are shown in Figure 5.9 – 5.12, in order to envisage the PM-driven oxidative reactants according to individual total mass and PM concentration on each of the collected filters.

The results show a clear different pattern of PM $OP^{antioxidants}$ metrics between indoor-outdoor samples. Indoor PM OP ^{antioxidants} metrics was observed with reduction pattern throughout the monitoring campaign. However, outdoor PM OP ^{antioxidants} metrics was observed in constant value. The maximum indoor PM OP ^{antioxidants} μg^{-1} was 1.2 ± 0.1 for ascorbate and 0.9 ± 0.1 for glutathione, whereas, the minimum values were about 0.6 ± 0.2 and 0.3 ± 0.1, respectively. Further, the maximum indoor PM OP ^{antioxidants} m^{-3} was recorded at 75.5 ± 5.1 for ascorbate and 27.9 ± 6.3 for glutathione, and minimum values were 24.2 ± 3.5 for ascorbate and 19.8 ± 2.5 for glutathione.

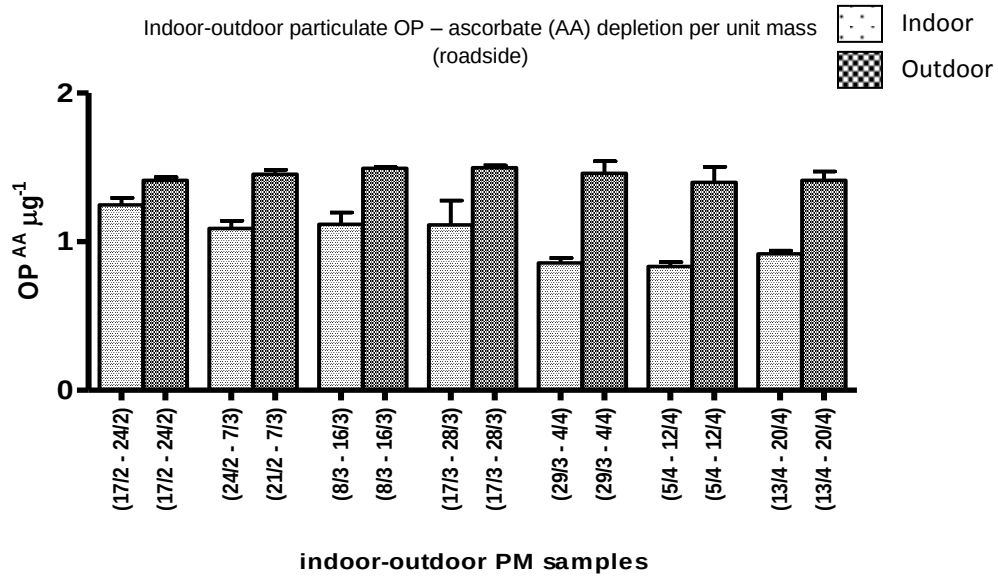


Figure 5.9: Oxidative particulate OP metric: AA depletion per unit mass between indoor and outdoor PM $_{TSP}$ from mechanically ventilated office building (roadside).

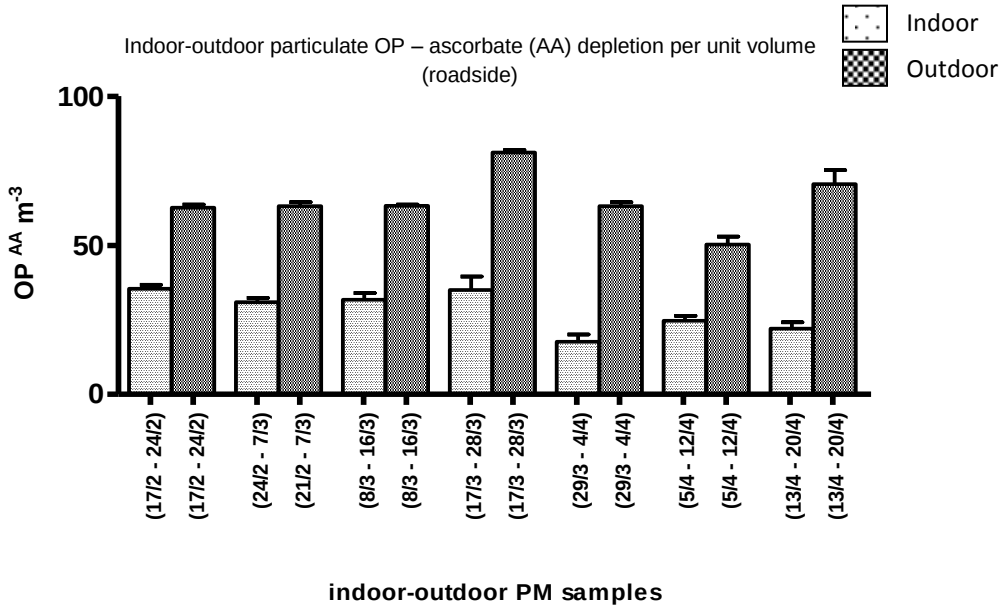


Figure 5.10: Oxidative particulate OP metric: AA depletion per unit volume between indoor and outdoor PM $_{TSP}$ from mechanically ventilated office building (roadside).

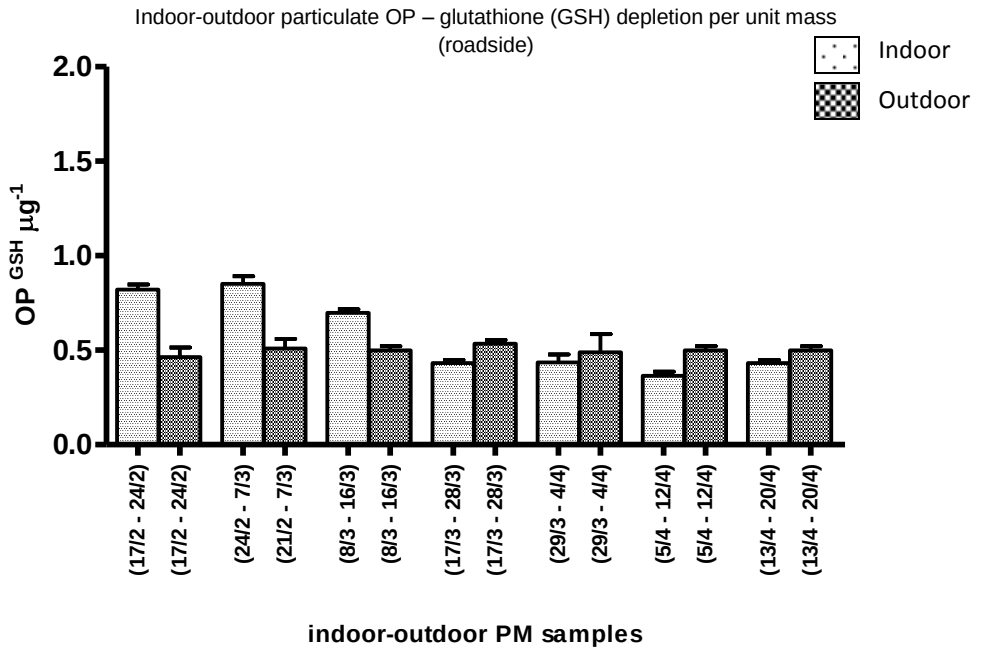


Figure 5.11: Oxidative particulate OP metric: GSH depletion per unit mass between indoor and outdoor PM $_{TSP}$ from mechanically ventilated office building (roadside).

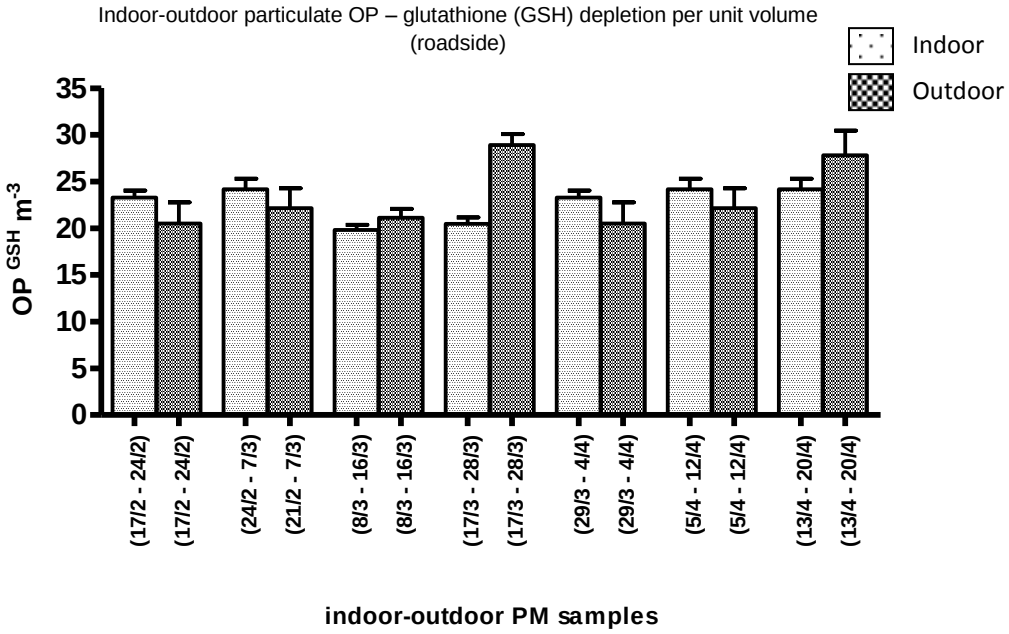


Figure 5.12: Oxidative particulate OP metric: GSH depletion per unit volume between indoor and outdoor PM $_{TSP}$ from mechanically ventilated office building (roadside).

Overall, Figure 5.13 shows the mean distribution PM OP metrics for ascorbate and glutathione after 3 months of observation. The outdoor PM OP^{AA} metrics were observed to be significantly higher than indoors, $p < 0.01$, mean 1.5 ± 0.33 for AA μg^{-1} and 62.3 ± 5.6 for AA m^{-3}, whereas for indoor OP^{AA} μg^{-1} and $OP^{AA}m^{-3}$, the mean was 0.98 ± 0.01 and 26.9 ± 5.2, respectively. However, there is no clear evidence to show any differences between indoor and outdoor PM OP^{GSH} metrics. The total average of indoor and outdoor $OP^{GSH}\mu g^{-1}$ was 0.48 ± 0.05 and OP ^{GSH} m^{-3} was 20.1 ± 2.6.

The two different patterns of PM OP metrics illustrated in these results were believed to be reflected by building design improvement effects – door upgradeswere carried out between 14th and 20thMarch 2011.In order to characterise the differences of PM-driven oxidative activity due to this building improvement, a control measure comparison study was undertaken, and is discussed in the next section.

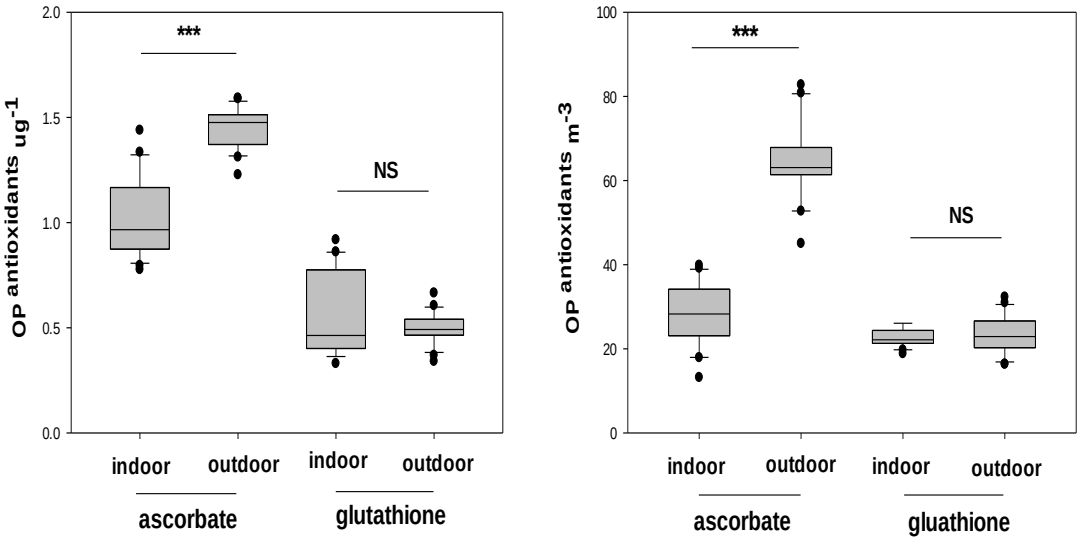


Figure 5.13: Oxidative particulate OP metric: AA and GSH depletion per unit mass and volume between indoor and outdoor PM TSP at mechanically ventilated office building (roadside site).

*Note: Statistical comparisons of the AA and GSH were performed using a one way ANOVA, with post hoc analysis performed using unpaired t-test. Where data has shown significant differences between indoor-outdoor PM samples for both OP antioxidant activity, *** is significant p-value less than 0.001 (indoor-outdoor OP ^{AA} m^{-3} = 0.005, indoor-outdoor OP ^{GSH} m^{-3} = 0.004).*

Control measures: The differences of PM OP due to building design improvement

After 1 week of improvement works, indoor and outdoor PM OP metrics were compared to characterise the changes due to building design improvement, particularly for indoor OP metrics. Figure 5.14 shows the mean distribution of indoor and outdoor PM OP metrics before and after the door upgrade.

Interestingly, the indoor PM OP^{AA} rate decreased significantly after the door upgrade, $p < 0.01$. The decrease in indoor mean $OP^{antioxidants}$ μg^{-1} was observed from 1.18 ± 0.13 to 0.86 ± 0.33, and OP^{GSH} μg^{-1} from 0.78 ± 0.15 to 0.41 ± 0.09. Furthermore, PM $OP^{antioxidants}$ m^{-3} showed a similar finding, where indoor OP^{AA} μg^{-1} and OP^{GSH} m^{-3} decreased from 36.8 ± 3.8 to 21.1 ± 2.6 and from 24.8 ± 2.1 to 21.2 ± 1.9, respectively. However, the mean outdoor value of PM OP for both antioxidants was constant throughout the control measures analysis. The significant reduction of indoor PM $OP^{antioxidants}$ after the door upgrade may indicate the total mass reactive composition was different, reflected by the building design improvement.

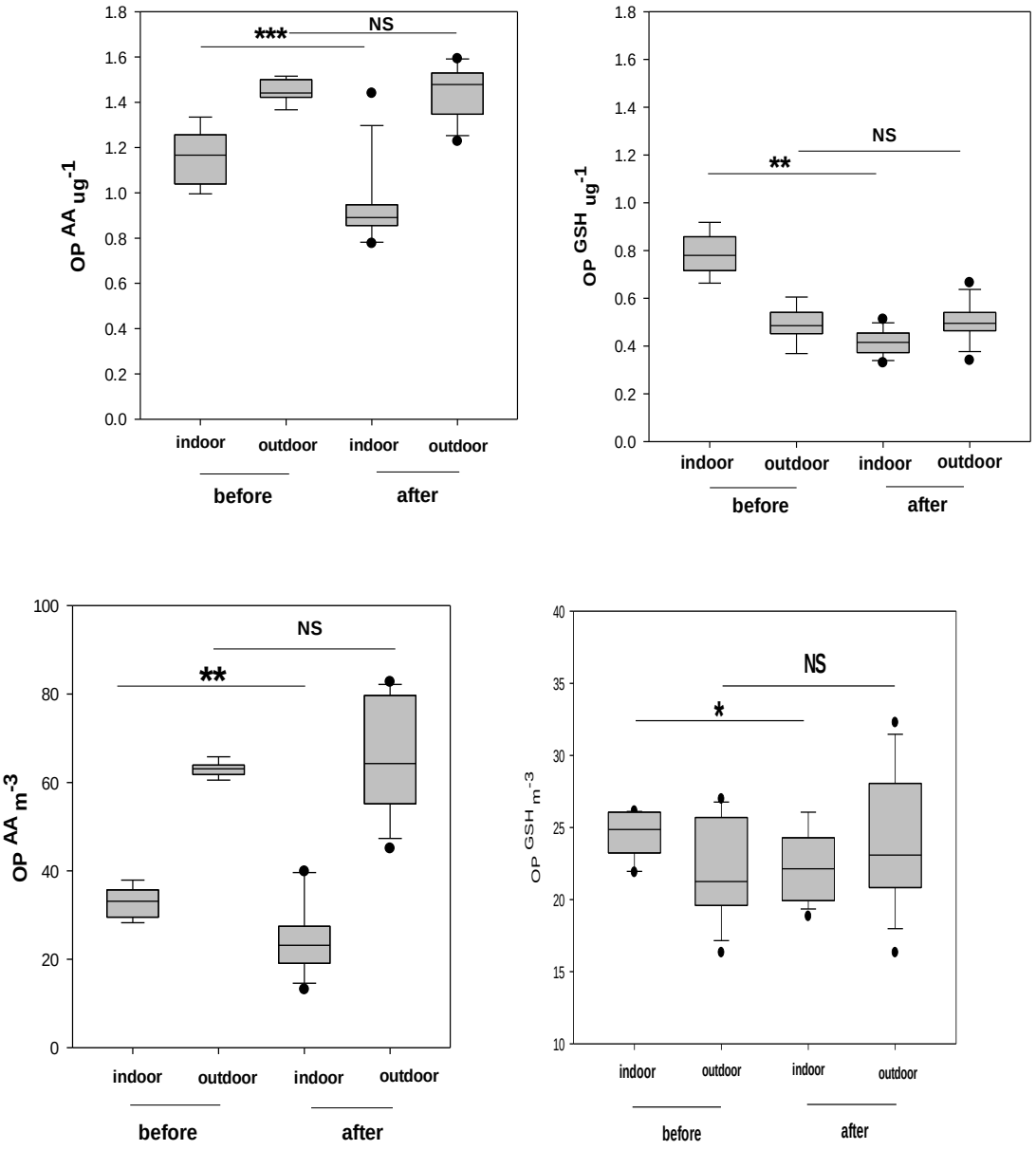


Figure 5.14: Mean oxidative particulate OP metric: AA and GSH depletion per unit mass and per unit volume between indoor and outdoor PM TSP from mechanically ventilated office building (roadside site).Data were separated into two observation periods between before and after the door upgrade.

*Note: Statistical comparisons of the AA and GSH were performed using a one way ANOVA, with post hoc analysis performed using unpaired t-test.** denotes significant p-value < 0.05 and *** p-value < 0.01.*

5.3 Discussion

This study presents the first continuous time series of OP measurements involving ambient and indoor PM samples, which cover two contrasting buildings in London (one at roadside and one at an urban background site). The unique dataset established in this study allows greater understanding of the variability and drivers of particle toxicity and, ultimately, helps to determine a closer association between health effects and particulate emission from both indoor and outdoor sources. The two OP metrics of oxidative activity are dependent on the reagents used, ascorbate and glutathione, and provide PM toxicity assessment of the indoor-outdoor PM over the filter's exposure period prior.

Generally, the mechanically ventilated office building at the roadside site was shown to have a higher PM OP depletion rate for both indoor and outdoor PM samples when compared to the naturally ventilated school building at the urban background site. This finding suggests a link between primary traffic-related pollutants and particle toxicity at the roadside site, which were also demonstrated in other studies (Park & Kim 2005, Vallius et al. 2005, Wessels et al. 2010, Kelly et al. 2011a). Furthermore, a number of recent studies also observed that PM samples from roadside sites show higher antioxidant depletion rates in ambient PM OP metrics, particularly in ascorbate(Godri et al. 2010a, Godri et al. 2010b, Kelly et al. 2011b). Godri and colleagues (2010a) suggested in their study that contributions from traffic emissions in London increase the concentration of redox cycling trace metals, which in turn cause a greater particulate oxidative burden. However, this study did not demonstrate an increment in PM OP at roadside sites compared to those situated away from major roads. The authors also recommended future work with longer-term sampling periods and a larger suite of analytes to better elucidate the determinants of PM OP and to more fully explore contrasts between site types. Further investigation in another study in the Netherlands (Boogaard et al. 2011) revealed that high contrast between busy streets and urban background locations in the same city were found to have higher levels of chromium, copper and iron (vehicle exhaust combustion – roadside), the majority of which was present in coarse fractionPM. This study also found a high contrast between black carbon (BC) and NO_X, which are typically indicators of direct combustion emissions. However, the contrasted findings in this study

are still too subjective to be conclusive without considering the detailed temporal and spatial oxidative potential characteristics from each of the study sites.

Naturally ventilated school building

Particulate oxidative activity, ($OP^{antioxidants}$ m^{-3}), shows a clear difference between indoor-outdoor PM samples with indoor PM OP observed to be significantly higher than outdoors. This suggests that the majority of high peak PM concentration derived from indoor sources was influenced by building occupancy, which could be attributed from various types of classroom activity. The results are consistent with previous measurements on diurnal variation profiles in Chapter III, section 2.3, where the high peak PM concentration was recorded during occupied periods, between 0900- 1300 hours. This accords well with previous studies discussed in Chapter III, section 3.7, which indicate that the majority of the high peak of PM mass and PM concentration were driven by building use (e.g. Alshitawi et al. 2011, Branis et al. 2005).

Nevertheless, it worth noting that the active building use also involved with opening doors (during rush hour) which might influence by the fluctuation concentration from outdoor PM contribution into the classroom. Such scenario could explain the absence of differences between both indoor-outdoor PM mass samples, $OP^{antioxidants}$ μg^{-1}. Thus, pertaining to this scenario, I would believe that the total mass reactive PM composition was not only influenced by building occupancy but also from outdoor contribution as well. This finding also cooperate with other study by Schwarze et al. 2006, the author conclude that the sources and the composition of PM in indoor air may differ from those in outdoor air. Further, by expanding the analysis to correlate between the PM-induced antioxidants AA and GSH, the strength of the association was improved when both antioxidant depletions were combined. This may indicate that a common PM component was driving the loss of these antioxidants.

To my best knowledge, no data on PM OP metrics have been presented in the literature to correlate between indoor and outdoor PM-induced antioxidants. However, it must be noted that other scientific studies were able to show a comparative trace metal indoor-outdoor PM analysis, which has a similar approach to demonstrating the PM toxicity. The

identification of chemical and morphological properties of PM in school classrooms and outdoor air (Fromme et al. 2008) revealed that 43% of $PM_{2.5}$ and 24% PM_{10} consisted of a sulphate composition of ambient origin. The composition of the classroom's PM (high calcium concentrations) and the findings from microscopic electrons suggest that the indoor PM consists mainly of earth crustal materials and also from building materials and chalk.

In addition, interestingly, when PM OP datasets were categorised and grouped as building occupancy dependent, the indoor PM $OP^{antioxidants}$ metric was found to have a higher depletion rate during occupied periods compared to unoccupied periods, particularly for ascorbate. However, OP^{GSH} μg^{-1} did not show any clear differences between those periods. This finding indicates PM_{TSP} composition may have different toxicity effects between the two antioxidants used. This would be in line with recent results demonstrating that the physical activity of the pupils leads to an increase in PM_{10}However, their findings support the hypothesis that indoor-generated PM may be less toxic compared to PM in ambient air (Fromme et al. 2008). This is maybe true to relate the total mass reactive composition is more related to the coarse particle ($PM_{2.5-10}$) or fine particle ($PM_{2.5}$) via certain type of classroom activity and penetration from ambient environment during occupied period, as showed in previous I/O PM ratio analysis – Figure 3.7 in Chapter III. The highly reactive of such particles has been proven inother study recently (Dinh et al. 2012); they found that the presence/absence PM_{10}ratio confirms the PM10 concentrations raise during children activities in the classroom. The children presence leads to an increase of elemental concentrations (ng m^{-3}) but does not influence the elemental distribution in the different particulate fractions, PM_{10} and $PM_{2.5}$. Further, the authors stressed that the trace elemental were enriched in the fine particle and crustal elements present higher concentration in the coarse fractions. However, the finding from this study also conclude that the consideration also should noted the indoor PM composition were differs depending on the school surroundings, such as mixed anthropogenic particle sources.Another study, by Morawska et al. (2009), also suggests the complexity of PM toxicity that occurs indoors may be influenced by secondary organic aerosols. This study revealed that the detergent used during cleaning activities in the school contributed monoterpene, and this was one of the main organic compounds.

The reactive interaction between organic compounds with O_3 (either from ambient or indoor environments) led to the formation of secondary organic aerosols.

With respect to seasonal variation analysis, indoor and outdoor OP^{AA} μg^{-1} was found to be significantly higher during winter seasons when compared to summer. This result supports the finding above, that the majority of the PM mass and concentration was observed during occupied periods; the increments were recorded during winter when the school children spent the majority of their time inside the classroom with indoor curricular activity. The high PM toxicity during winter seasons was also illustrated in a study by Valavanidis et al. (2006), where a seasonal effect was observed for the size distribution of aerosol mass, with a shift to larger fine particles in winter seasons. The most commonly detected trace metals in the TSP samples during these periods were Fe, Pb, Zn, Cu, Cr, V, Ni and Cd. It is worth noting that this study took place in heavily polluted urban areas with other anthropogenic emissions. The results of this study also underlined the importance of local emission sources, especially diesel used by central heating during winter seasons.

Mechanically ventilated office building

A clear difference between indoor and outdoor PM OP at this site indicates that PM composition differed at this location. However, as two different types of instruments and filters were compared at this site, a direct comparison of outdoor PM OP and indoor PM OP is not possible. The most obvious explanation for these results is the direct link of active PM composition with local vehicular emissions. A study to identify the chemical characteristics and oxidative potential of PM emissions from gasoline, diesel and biodiesel cars suggesting that the diesel and gasoline vehicles produced the most potent exhaust in terms of oxidative activity (Cheung et al. 2009). An extended version of this study discovered that soluble Fe is strongly associated with particulate reactive oxygen species (ROS) activity, R = 0.99. The authors also suggest that incomplete combustion of lube oil emissions might be an important driving factor of overall PM-induced oxidative stress (Cheung et al. 2010). Indeed, diesel exhaust tended to express very high ROS potentials, and was demonstrated as linked with secondary organic aerosols from an α-pinene + toluene + an urban hydrocarbon mixture giving the highest ROS response

(Rattanavaraha et al. 2011). Supporting evidence from another study by Biswas et al. (2009) also suggests that the semivolatile fraction of particles are far more oxidative in nature rather than refractory particles. These authors also stress that an increase in atmospheric dilution (previous tunnel and ambient studies) will reduce PM oxidative activity.

In addition, a RAPTES project that examined in vitro toxicity of PM collected at different sites in the Netherlands, including roadside and urban background sites, revealed that most of the PM samples induced a concentration-dependent decrease in MTT-reduction activity and an increase in pro-inflammatory markers, with the exception of the urban background site. Their results were consistent with other investigations showing that chemical compositions as well as oxidative potential are determinants of PM-induced toxicity *in vitro*(Steenhof et al. 2011).

Interestingly, the building design improvement in this study, consisting of a door upgrade, highlighted the most important finding from this site. The indoor OP^{AA} depletion rate was reduced significantly when before and after control measurement periods were compared. This suggests that the reactive composition was reduced due to the building design improvement. The poor design of the door at the main entrance of this building – identified by small gaps, and discussed in Chapter IV, section 4.5 – most likely allowed reactive-traffic-derived PM to be blown into the building. Again, this finding suggests that the traffic emission sources play a relatively important role in determining PM OP activity. There are other possible influenced factors to be considered which is not identified prior to this particularly finding, such as the differences of meteorological condition (wind speed and direction) between before and after the doors upgrade. Due to the short term regimes within the period of the building design improvement in this study, the analysis is not included.

5.4 Limitations

This study established a unique PM OP metric database. Most of the findings in this study linked PM-induced antioxidant depletion with building occupancy. However, there are known limitations to the sampler-based technique; for instance, filter handling and conditioning can introduce errors. Also, it may involve a loss of semi-volatile compounds in PM samples while travelling between site and laboratory for further PM OP analysis.

One of the main limitations for PM OP analysis is the required PM mass of at least 0.5 mg, which only allows the filter collection and occupancy diaries to be summarised in weekly/biweekly observation. Further, due to the low flow rate instrument involved in this study, most filter exposure was not able to capture the required PM mass in the shorter average periods. Indeed, it is also useful to recall that the type of classroom activity (during occupied periods) was varied within those periods. Thus, the findings in this study do not represent the actual building activity occurring on a daily basis.

A logical step to expand upon this section of the research would be to simultaneously record airborne particulate concentration into different sized fractions (to separate the filter PM samples collection: PM_{10} and $PM_{2.5}$) using different filter inlets and a high flow rate instrument in relatively shorter average periods of filter exposure (i.e. on a daily basis).

5.5 Conclusion

This study demonstrated that oxidative activity in the context of particulate metrics, from both internal and external sources, is a useful tool to illustrate any source changes in the transfer of pollutants into buildings. The two sites showed a clear difference in PM_{TSP} $OP^{antioxidants}$ metrics, particularly the indoor OP metrics in the roadside building. This may explain the high reactive PM composition attributed from outdoor vehicle combustion.

In the naturally ventilated school building, the similarity between indoor and outdoor PM OP^{AA} μg^{-1} observed may explain the transport of outdoor pollutants into a building. This

finding is also supported by correlation analysis, $r = 0.56$ with $p < 0.05$, leading to a hypothesis that a similar component was driving the loss of these two oxidants. Additionally, the variability between indoor and outdoor PM OP ^{antioxidants} m^{-3} was driven by the individual building occupancy diary. Further, the majority of reactive PM composition trapped inside the building when the windows were closed during winter might play an important role in the increment of oxidant loss, particularly in ascorbate concentration.

The most important finding in the mechanically ventilated office building at the roadside site was the significant decrease in indoor PM induced antioxidant depletion, observed after the door improvements. This finding highlights the importance of building design in providing a better indoor environment, particularly for buildings adjacent to busy roads.

Chapter VI

Discussion

6.1 Introduction

Poor IAQ has been related to increases in sick building syndrome and respiratory illnesses as well as losses in productivity and performances in offices and schools (Burge 1992, Burge 2004). Growing scientific evidence has indicated that the indoor air within building premises can be more seriously polluted than the outdoor air (Yu et al. 2008, Eick & Richardson 2011). However, poor building design and lack of ventilation system will contribute to the ingress of outdoor pollution into the indoor environment, where occupant exposure is likely to be high. Currently, there is still lack of evidence and understanding of indoor-outdoor air pollution issues within the building design community. Hence, this thesis provides reasonable information to envisage the impact of outdoor pollution sources on indoor microenvironments by looking at into two extreme scenarios of building types and location.

6.2 Discussion

There are two chapters involved in this thesis being observed and discussed separately, the relationship of indoor-outdoor pollutants concentration according to its specific location and building types. The study aims and objectives approaches in each of these chapters were similar. However, new interesting results and some expansion of the descriptive analysis described in this thesis showed that the ingress of outdoor pollution contribution in poor IAQ were also driven by other factors such as building orientation, occupancy and different set of energy use which also correlates to each other.

Thus, this chapter was designed to discuss and to link those findings referring to the study aims and objectives by comparing the two study sites:

a. The establishment of paired long-term indoor-outdoor pollutant monitoring in this study revealed that the pollutants concentration were differed depending on its building types and locations:

Indoor-outdoor NO_X, NO_2 and O_3 concentration

An extreme indoor concentration of indoor NO_X and NO_2 monitored in mechanically ventilated office at roadside site during rush hour on working-days were significantly dependent on the degree of exposure to the heavy-trafficked emission. Further, the fact that the door upgrade did not solve the high NO_2 problem (as shown in the control measure study) shows that even small breaks in the building envelopes can allow ingress of large volumes of outdoor pollutants penetration. This finding highlights the same conclusion stated in other studies which proposed the impact of local pollution transportation indoors due to the penetration and/or infiltration, particularly via vehicle emission in urban environment (Chen et al 2010, Hayashi et al. 2002, Bady et al. 2008). It was also revealed that the importance of air tightness of a building has a strong impact on the penetration of outdoor gaseous pollutants into the building without absorption (Hamdy et al. 2010). However, this finding contradicts to the other case of study. The high indoor NO_X concentration which was observed during unoccupied period in naturally ventilated school building reacted to the indoor source. This finding may not be applicable to other similar building and locations that have no such source. Interestingly, the increment of indoor O_3 observed in school was linked to the outdoor penetration, particularly during occupied period.

Indoor-outdoor PM_{10} and $PM_{2.5}$ concentration

In naturally ventilated school building, the increment of the indoor PM_{10} was attributed to the building used and occupancy. The peak concentration identified clearly to be linked from certain type of classroom activity, particularly in coarse particle ($PM_{2.5-10}$). However, a greater proportion of indoor $PM_{2.5}$ was contributed from outdoors. These findings also react similarly to the other site of cases, particularly for the PM_{10} which was correlated to the opened doors during occupied period at the building entrance. Interestingly, the local peak indoor PM concentration

was shown in similar range with other studies such as Branis et al. (2005) and Branis&Safranek (2011). A recent study done by Wang et al. (2010) to characterise ultrafine particle inside and outside commercial buildings in long term regimes – this study found similar pattern of I/O ratios which the number is generallyincreased with particle size. Nevertheless, the increment of indoor PM was also to be linked to the outdoor contribution, as showed in the expansion study at this site. The PM concentration showed a clear reduction pattern after the door upgrade throughout the measurement periods, mean differences of concentration improved from -10 µg $m^{-3}$to 10 µg m^{-3}. The reduction of indoor PM concentration via elimination of penetration factors was proven in this part of study, however, it cannot be relied upon one factor and must be related to other natural factors which was not identified in this study, such as temperature differences inside and outside a building (Ni Riain et al. 2003).

b. The differences of indoor-outdoor pollutants concentration according to meteorological condition (wind speed and direction):

Indoor-outdoor gaseous pollutants (NO_X, NO_2 and O_3) & particulate matters (PM_{10} and $PM_{2.5}$) concentrations

The qualitative assessment via polar frequency plot analysis supports the significant effect on transferring pollutants outdoor into indoors at the roadside site was also derived by meteorological conditions (wind speed and direction). This is most likely driven by local pollution sources due to its location within building street canyon orientation. This part of the finding shows that the impact of street canyon orientation was proven to be affected by wind ventilation performance, and in lined with other studies as well (Bady et al. 2006 and Bady et al. 2011). However, a strong conclusion cannot be made by relying on this assumption. There are other factors (which are not considered in this study) to be looked into detail (Buccolieri et al. 2010), such as the actual height-width measurement of the building / density, wind flow and ventilation rate within building envelopes in different scenarios (close and opening entrance of doors). In contrast, the results in the other site did not show any clear evidence that the influence of wind speed and direction to cause the transportation of outdoor pollutant into indoors. Due to the assumption mentioned above and some aspect of

limitation in this study, the conclusion is not considered as definite. Further, the present meteorological data that was available from Bexley 2 used in this study is not consideredas representing local meteorological condition for each study sites. Moreover, AER, which are specified as major limitation in this study, might be useful to consider in order to fully understanding the transfer of outdoor pollutants indoors.

c. The differences of indoor-outdoor pollutants concentration according to building use (occupancy):

The fluctuation of indoor-outdoor pollutant concentration which was observed in the long term monitoring database could lead to various influence factors. These factors being narrowed down by looking into short term regimes via diurnal variation profile into 4 measurements time periods (occupied, partially occupied, weekend and public holiday).

Indoor-outdoor NO_X, NO_2 and O_3 concentration

In general, the indoor-outdoor gaseous pollutants concentration was reflected differently at each of the site campaigns. Due to the fact that the indoor NO concentration in the classroom was possibly dominated by indoor source, it presence was also believe to play an important role of reducing O_3 in the classroom. However, the widely variable building occupancy as showed in previous analysis means that this would have limited application, such as the determination of AER and indoor chemistry which are not determined in this study. Zhang &Lioy (1994) has stated in their study the importance of AER in the elevation of indoor O_3 and rapid reaction of O_3 (sun light radiation) particularly during summer time. On the other hand, for mechanically ventilated office building at roadside site, most of the indoor NO_X proportion was attributed from outdoor concentration particularly during occupied period. The concentration was getting higher during night time.This pattern of concentration may possibly be explained by a lack of ventilation inside the building, and indoor pollutants contributed from outdoor sources due to infiltration of the building envelope. The reduction of indoor pollutant concentration particularly

duringthe weekend after the door upgrade demonstrate air tightness, and gave building envelopes a good protection from the direct external sources.

Indoor-outdoor PM_{10} and $PM_{2.5}$ concentration

The diurnal variation profile analysis clearly shows that indoor PM concentration was influenced by occupancy, particularly for the larger particle. However, the building use (occupancy) was differed depending on occupant's movement such as classroom activity and opening doors during rush hour. Thus, the consideration of outdoor penetration should be noted as one of the influenced factors, particularly for $PM_{2.5}$.

d. The differences of indoor-outdoor pollutants concentration according to seasonal variation:

The building's location and ventilation types provide a way for outdoor pollutants to penetrate or to be transported into indoors. The building occupants' behaviour (opening/closing doors or windows) and also temperature differences (due to central heating and temperature adjustment) between seasons may reflect the negative-positive pressure to initiate indoor-outdoor pollutant interchange concentration within building envelopes. The analyses showed in the previous chapters indicate that the penetration of certain outdoor gaseous pollutants into indoors occurred during summer time due to thermal comfort. For example, O_3 (naturally ventilated school building) and NO_X& NO_2 (mechanically ventilated office building). This is also similar to PM concentration, particularly for PM_{10} (only one site available – naturally ventilated school building). However, there is no correlation that has been observed between seasons for all pollutants species throughout the monitoring campaigns. It may be reflected to the other missing important information to be noted as one of thelimitation in this study, such as AER due to opening inlets (windows/doors) between seasons which would explain better the interchange rate of outdoor pollutants into the building.

e. The differences in PM-induced oxidative activity between indoor and outdoor at two study campaign buildings:

The results from the long term indoor-outdoor pollutant monitoring dataset also supports by the PM OP analysis to demonstrate oxidative activity in the context of particulate metrics, from both internal and external sources. The two sites represent two different cases showed a clear difference in PM_{TSP} OP ^{antioxidants} metrics. Generally, the mechanically ventilated office building at the roadside site showed a higher PM OP depletion rate for both indoor and outdoor PM samples when compared to the naturally ventilated school building at the urban background site. However, interestingly when indoor OP metrics between two sites were compared, OP metrics in the office building recorded higher depletion rates compared to school building. In addition, when PM OP dataset were categorised and grouped as building occupancy dependent, the indoor PM OP antioxidants metrics was found to have a higher depletion rate during occupied period. With respect to PM OP activity and seasonality, PM OP metrics were found to be significantly higher during winter seasons, which particularly in particulate mass metric.

The main influence factor to explain these results is the direct link of active PM composition with local source contribution. These findings suggest a link between particulate reactive composition from traffic-related pollutants (roadside site) and also from the particle toxicity via indoor activity (urban background) particularly during occupied period.However, due to the fact that most of the PM TSP exposure was not able to capture the required PM mass (less than 0.5 mg) in the shorter period, these findings do not represent the actual exposure on a daily basis.

6.3 Conclusion

This unique dataset and findings highlights the complexity of internal-external air quality relationship within building envelopes. Returning to the hypothesis and research questions posed at the beginning of this study, it is now possible to state that the ingress of outdoor pollution contribution in poor IAQ differs according to its driven local source

and set of building ventilation use. Interestingly, other influence factors also involved such as dispersion of pollutants within street canyon building (roadside site), the complexity of building occupancy (urban background site) and different set of energy use.

The linkage of indoor-outdoor pollutants relationship found in this study and also have been elaborated in this chapter, are being summarised in the conceptual framework as shown in Figure 6.1 and 6.2. Specifically, Figure 6.1 is drawn to mind-mapping the study parameters involved in this study and also the possible pathways contributors of outdoor pollutants into indoors. The possible pathways factors are differed according to the building location and ventilation types. These factors are identified (colored boxes) as study parameters and hypothesised as the study aims and objectives, as below:

a. **Grey box:** driven factors involved in this study (meteorological condition, pollutants source, building use, building envelopes and pollutant toxicity – PM)
b. **Blue box:** pollutant parameters involved (such as NO_X, NO_2, O_3 and PM) from both indoor and outdoor environments.
c. **White box:** external driven factors which are not identified in this study. The assumption and consideration from these factors are important for conclusive hypothesis.

Figure 6.2 is simplified in a similar way by a conceptual framework as below in order to identify the main findings hypothesised in this study and to clarify the aims and objectives which have been met. The framework also identified other influenced factors (**green box**) which are not identified in this study, but are crucial for holistic approach for conclusive hypothesis. It is worth noting that the involvement of other biases in this study such as methodological assumptions and limitation which are stated in previous chapters and also has been identified as further recommendation which will be discussed in the next chapter.

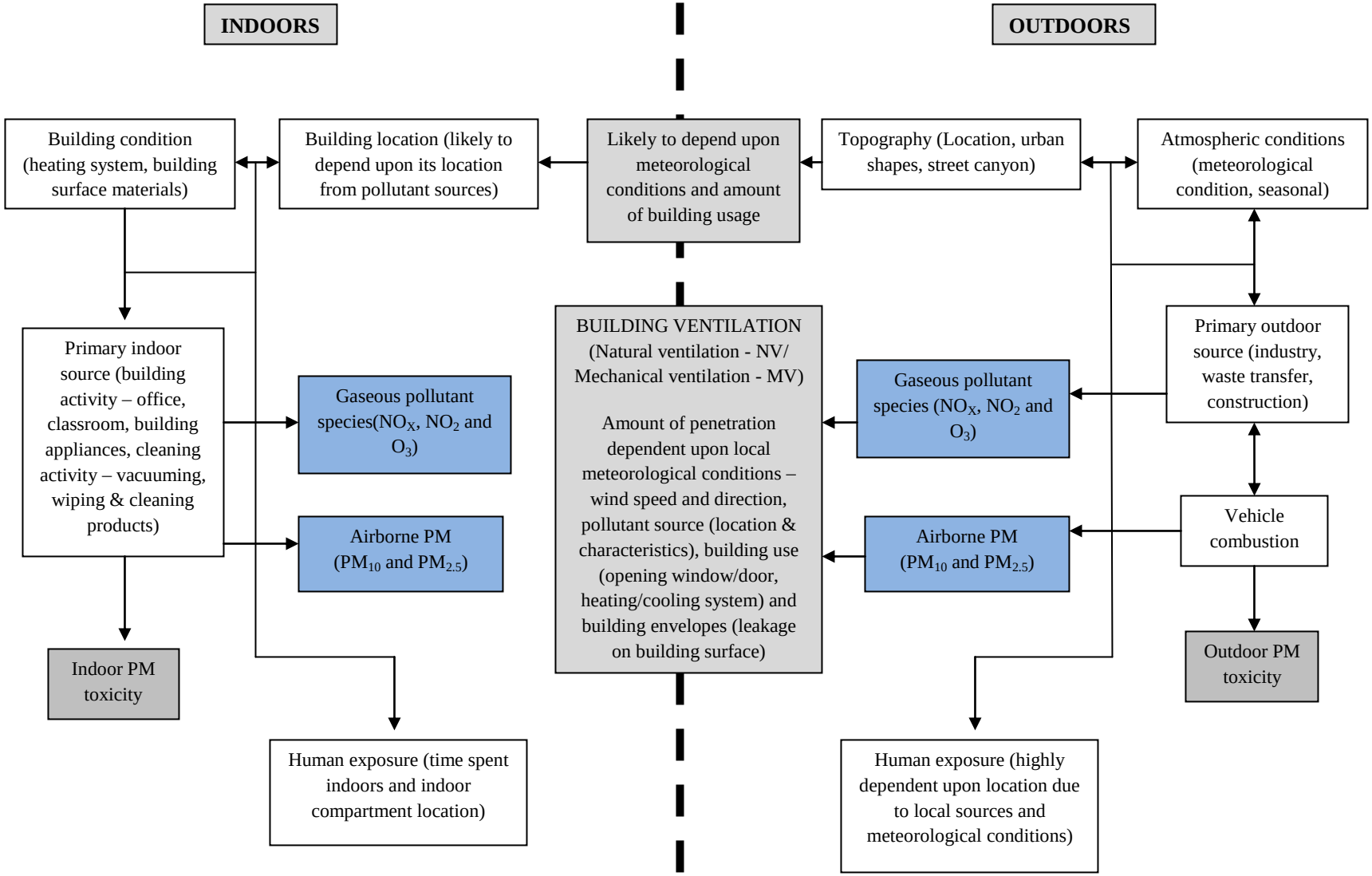


Figure 6.1: Conceptual framework of indoor and outdoor pollutant pathways in different building location and ventilation types.

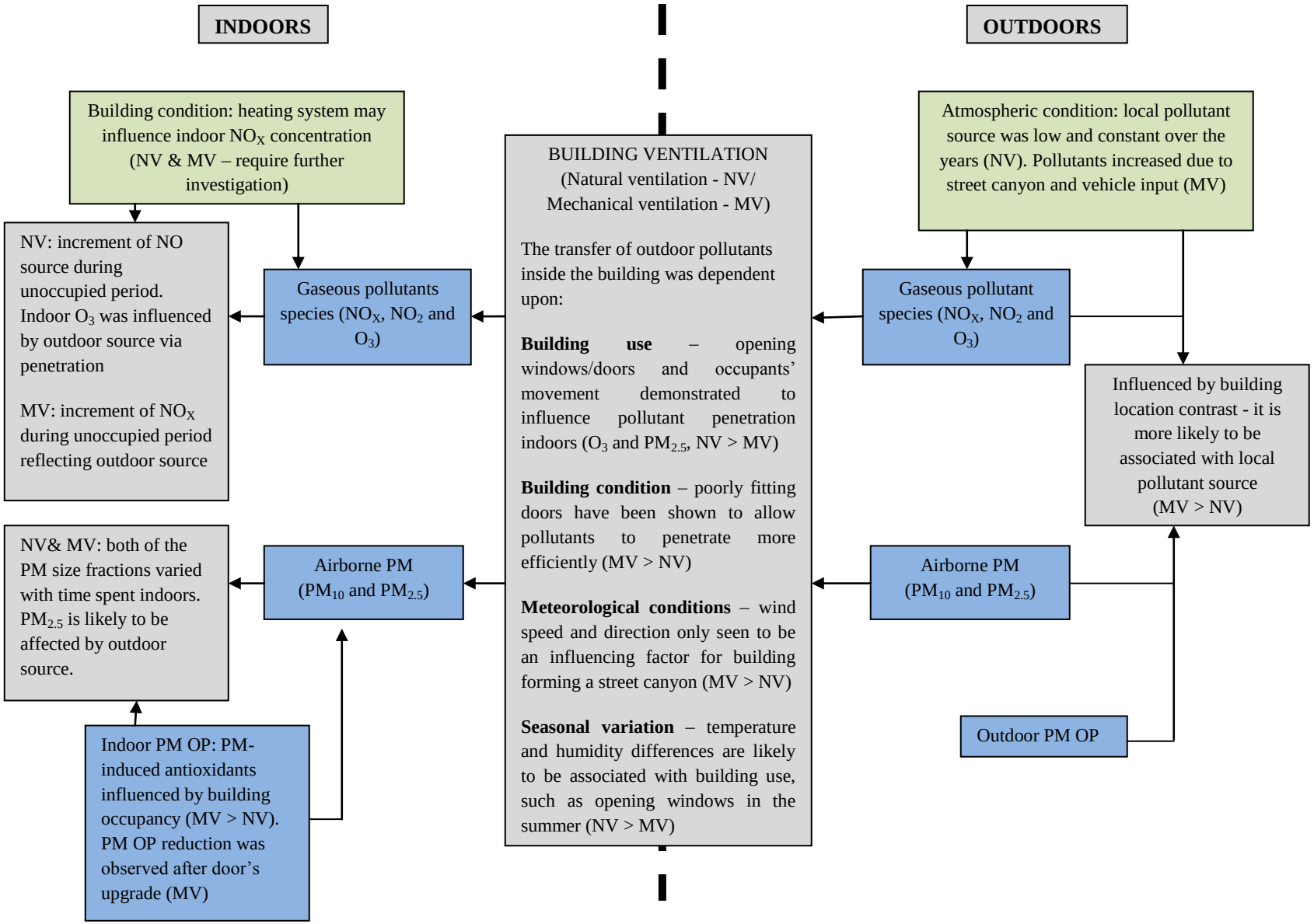


Figure 6.2: Conceptual framework showing possible pathways identified by this research.

Chapter VII

Summary and Recommendations

7.1 Summary

This study involved the long term monitoring of gaseous pollutants (NO_X, NO_2 and O_3) and PM (PM_{10} and $PM_{2.5}$) at two contrasting building types and location within London. The measurement over a long time period established in this study allows greater understanding of the pollutants transfer over a wide range of meteorological and seasonal condition. The resulting database is also utilised to assess the differences caused by changes in building use and occupancy. The unique dataset in this study also presents the novel measurements involving continuous time series PM OP analysis from both indoor and ambient PM samples. The two OP metrics of oxidative activity represent in this dataset are dependent on the reagent used, ascorbate and glutathione, and provide PM toxicity assessment of the indoor-outdoor PM over the filter's exposure period prior. The combination of these measurement perspectives ultimately help to determine a closer association between health effects and pollutants emission from both indoor and outdoor sources. The two selected sites involved in this study representing two typical building scenarios in London, school and office. However, the differences in ambient pollutant exposure between sites may have different impacts on building dwellers.

The summary listed below is to highlight the major findings of this study according to the each chapter:

Case 1- Naturally ventilated school building (roadside site):

- Typically, outdoor air in urban areas are usually at its highest concentration and IAQ inside buildings draws from ambient air particularly in a naturally ventilated building.

- However, paired long term monitoring in naturally ventilated school building in this study revealed that the indoor NO_X and O_3 concentration reacted differently according to seasonal, building used and occupancy.
- Due to the fact that indoor NO concentration in the classroom was possibly dominated by indoor source, it presence was also believe to play an important role of reducing O_3 in the classroom which were mainly came attributed from outdoors during summer time.
- The increment of indoor larger (PM_{10}) and coarse particle ($PM_{2.5-10}$) were attributed when the building was actively used and identified to be linked from certain type of classroom activity. However, a greater proportion of indoor $PM_{2.5}$ was contributed from outdoors.

Case 2 – Mechanically ventilated office building (urban background site):

- The monitoring database revealed that the distribution of indoor and outdoor pollutants located close to significant sources of pollution varied substantially and consistently with natural drivers of ventilation, particularly meteorological conditions, and dependent on the degree of exposure to the ambient environment.
- An extreme indoor concentration of indoor NO_X and NO_2 monitored during rush hour on working-days were explained by the lack of ventilation inside the building.
- Further, the fact that the door upgrade did not solve the high NO_2 problem (as shown in the control measure study) shows that even small breaks in the building envelopes can allow ingress of large volumes of outdoor pollution.
- However, interestingly, the PM concentration showed a clear reduction pattern after the door upgrade. The weekly variation profiledemonstrated positive reduction was observed after door upgrade throughout the measurement periods, with mean differences of concentration improved from -10 $\mu g\ m^{-3}$to 10 $\mu g\ m^{-3}$.

Characteristics of indoor-outdoor particulate oxidative activity in two contrasting cases in above:

- The two sites represent two different cases showed a clear difference in PM_{TSP} $OP^{antioxidants}$ metrics. Indoor OP metrics in the roadside building recorded higher depletion rates compared to the urban background site.
- At urban background site, when indoor OP dataset were categorised and grouped as building occupancy and seasonal dependent, the indoor PM OP antioxidants metrics was found to have a higher depletion rate during occupied period and was observed during winter time, which particularly in particulate mass metric.
- At roadside site, interestingly, a significant decrease in PM-induced antioxidant depletion indoors, observed after the door upgrade.

7.2 Research impacts

In general, the issue of IAQ has been largely overshadowed by the attention focused on ambient pollution. Due to the fact that most people spent their time indoors, there is no doubt; no question longer that the extent and depth of contamination in the air that we breathe is serious. As outlined conclusion in statements above, this study demonstrated the importance of building design and proper ventilation in providing a better indoor environment to reduce human exposure.

As highlighted in this study, the improvement of building designs and awareness amongst building designers was not the only practical ways to address IAQ issues, holistic approach via policy and regulations will make a huge impacts into the emerging concern to create so called ‘green buildings’ and sustainable design’ for healthy living environments. For instance, the regulation authorities could enforce greater emphasis on ventilation and the quality of the outdoor air, or set air quality standard for common indoor air pollutants. To date, a common indoor pollutant such as indoor airborne PM has not yet been effectively established. The high increment of indoor PM demonstrated in the classrooms in this study to be noted as clear need information to produce relevant evidence to undertake progressive action by the regulators.

7.3 Recommendations for future work

There appear to be other factors influencing the indoor-outdoor pollutant relationship that were not identified during this research, possibly associated with *ventilation rate, building air-tightness, building heating and door and window opening measurements,*which could not be controlled during monitoring. Due to installation difficulties and cost restrictions, some of these crucial parameters were not undertaken in this research. This study managed to compile long-term high quality monitoring data simultaneously. On top of that, this research was able to merge monitoring data with building diary activity. However, a more holistic approach using the parameters recommended above would be ideal to envisage the complex internal-external air quality relationships within building envelopes.

Currently, large advances have been made in indoor air exposure models used to determine the relationship between pollutant emissions and personal exposure. The application of a monitoring database in this study using such a model would allow greater understanding of estimation measurement on actual personal health exposure via internal and external air pollutant sources. This application could also be used to evaluate such indoor air chemistry models; involving some of the exotic species such as radicals would be highly beneficial for the models' validation.

Further, to ensure that the significant differences observed in this study are not an isolated phenomenon, a wider variety of locations is required to enable further analysis of spatial and temporal variation.

This study included a novel use of continuous time series of OP measurements involving ambient and indoor PM samples. The unique dataset established in this study could be extended for further oxidative assessment analyses, particularly in trace metal analysis. This analysis would allow greater understanding of the variability and drivers of active particle composition between internal and external sources and, ultimately, help to determine a closer association between health effects and particulate emissions.

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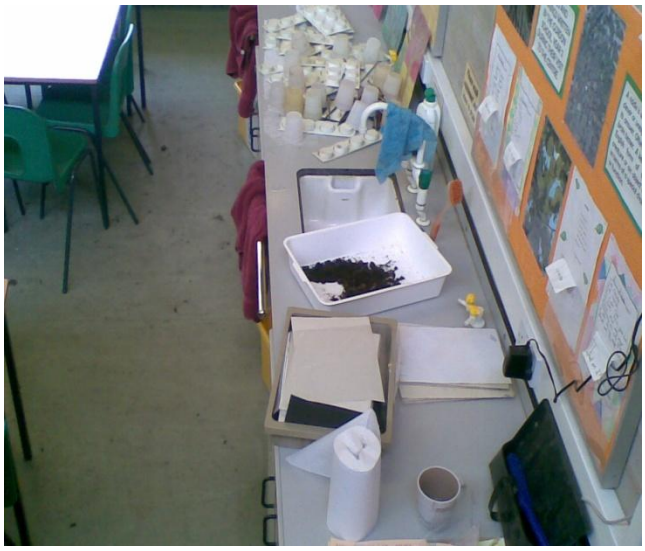
APPENDIX A: An assessment of indoor-outdoor pollutant at naturally ventilated school building – urban background

A.1 Site and sampling description (Sampling inlets and material used during classroom activity)

Indoor

Outdoor



Soil & insect (garden material) and paper making

Figure A.1: Indoor and outdoor sampling inlets at naturally ventilated school building (urban background) and one of the materials used during classroom activity.

A.2 Building diary activity (based on PM filter collection)

The occupancy usually changed every second hour according to class schedules and a short 20 minutes for lunch break during mid-day. The presence of students was quantified by means of a personal-hour indicator, which was calculated by multiplying the number of students by time in hours of their presence in the classroom (Branis et al., 2005). The average number of student-hours per the 7 hours high occupancy period was 105 (a maximum of 210 and a minimum of 70).

Table A.1: Date of filter collection and PM mass obtained according to building characteristics from naturally ventilated school building

Filter exposure period	Building occupancy & No of occupants *	Classroom activity **	Mass obtained from	Absolute Mass (mg)	Indoor/Outdoor mass ratio
9-16 Mar *(1 week)*	Occupied 25	Paper painting Soil & Insects	Indoor	0.91	4.14
			Outdoor	0.22	
17-24 Mar *(1 week)*	Occupied 24	Paper painting Quiz	Indoor	0.63	3.00
			Outdoor	0.21	
24-30 Mar *(1 week)*	Occupied 15	Briefing Outdoor	Indoor	0.47	1.09
			Outdoor	0.43	
30 Mar-6 Apr *(2 weeks)*	Partially occupied 4		Indoor	0.33	1.65
			Outdoor	0.20	
7-20 Apr *(2 weeks)*	Partially occupied 4		Indoor	0.85	1.16
			Outdoor	0.73	
20 Apr-4 May *(2 weeks)*	Occupied 21	Briefing Outdoor	Indoor	0.64	1.36
			Outdoor	0.47	
4-19 May *(2 weeks)*	Occupied 23	Briefing Outdoor	Indoor	1.28	1.47
			Outdoor	0.87	
19 May-1 June *(2 weeks)*	Occupied 22	Briefing Outdoor	Indoor	1.72	1.23
			Outdoor	1.39	
1 June-14 June *(2 weeks)*	Partially occupied 4		Indoor	1.91	0.62
			Outdoor	1.45	
14 June-29 June *(2 weeks)*	Occupied 33	Paper painting Outdoor	Indoor	2.35	2.50
			Outdoor	0.94	
29 June-15 July *(2 weeks)*	Occupied 21	Soil & Insects Outdoor	Indoor	1.35	2.11
			Outdoor	0.50	
15-27 July *(2 weeks)*	Partially occupied 4		Indoor	0.61	1.83
			Outdoor	0.50	
27 Jul- 10 Aug *(2 weeks)*	School Holiday		Indoor	0.62	1.66
			Outdoor	0.50	
10 Aug-26 Aug *(2 weeks)*	School Holiday		Indoor	0.65	1.52
			Outdoor	0.50	

Exposure Period	Building occupancy & No of occupants *	Classroom activity **	Mass obtained from	Absolute Mass (mg)	Indoor/Outdoor mass ratio
2 Sept-19 Oct *(2 weeks)*	Occupied 22	Soil Outdoor	Indoor	1.20	1.11
			Outdoor	1.08	
20 Oct -3 Nov *(2 weeks)*	Occupied 23	Soil & Insects Outdoor	Indoor	0.58	1.26
			Outdoor	0.46	
4- 15 Nov *(2 weeks)*	Occupied 33	Paper painting Quiz	Indoor	0.67	1.76
			Outdoor	0.38	
16 Nov-7 Dec *(2 weeks)*	Occupied 31	Soil & Insects Paper painting	Indoor	0.67	1.76
			Outdoor	0.38	
8-21 Dec *(3 weeks)*	School Holiday		Indoor	0.87	1.77
			Outdoor	0.49	
22 Dec – 12 Jan (2 weeks)	School Holiday		Indoor	0.49	1.40
			Outdoor	0.35	
13-27 Jan *(2 weeks)*	Partially occupied 4		Indoor	0.53	0.77
			Outdoor	0.69	
28 Jan- 8 Feb *(2 weeks)*	Snow		Indoor	0.92	1.74
			Outdoor	0.53	
9-23 Feb *(2 weeks)*	Occupied 11	Paper painting Briefing	Indoor	1.79	3.38
			Outdoor	0.53	
24 Feb- 9 Mar *(2 weeks)*	Partially occupied 8	Visitor	Indoor	1.40	1.52
			Outdoor	0.92	
10- 24 Mar *(2 weeks)*	Occupied 15	Paper painting Outdoor	Indoor	1.90	4.13
			Outdoor	0.46	

A.3 Long term indoor-outdoor monitoring database

Monitoring at this site ran from August 2008 until June 2011, including one year monitoring of airborne particulate matter began on March 2010 until March 2011. Data summary analysis was capture from analysers and data analysed using R statistical graphical plot.

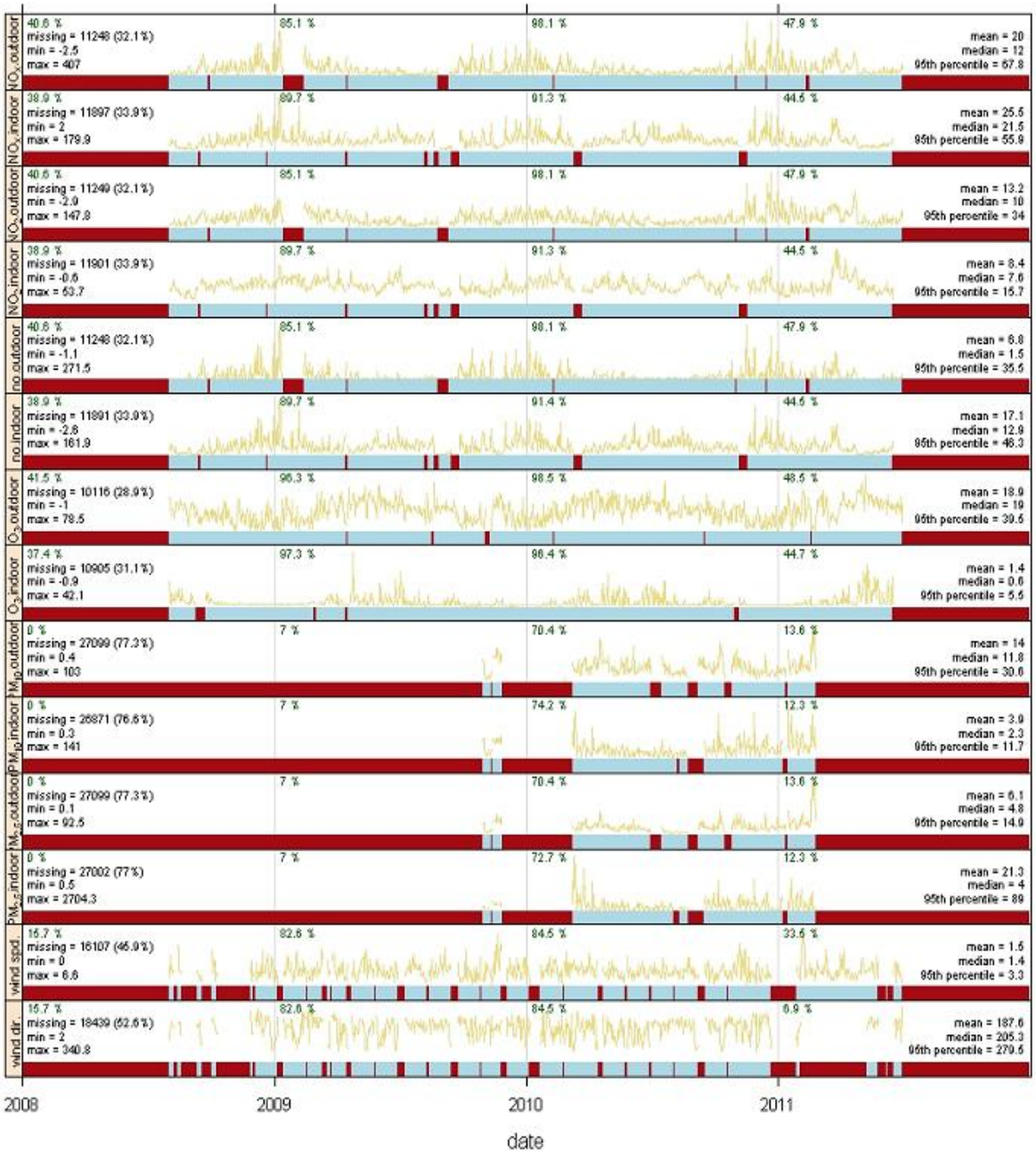


Figure A.2: Data summary plot for indoor-outdoor gaseous pollutants & particulate matter species monitored from August 2008 until June 2011

A.4 Indoor-outdoor source prediction (vehicle combustion)

In order to investigate the effect of vehicle combustion, indoor and outdoor average ratio were calculated. The concentration and correlation of indoor NO_2 was much lower than outdoor. Ironically, indoor NOx levels were higher than outdoor especially during weekend. This situation suggests an indoor NOx source derived from increased of indoor NO levels or indoor air chemistry inside the classroom. By comparing the indoor source ratio for I/O NO_2:NOx a weak correlation (R^2=0.0002) indicates very low indoor vehicle combustion sources from outdoor.

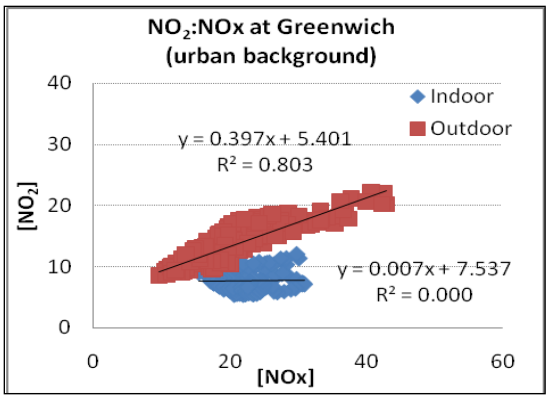


Figure A.3: Ratio mean nitrogen dioxide (NO_2): nitrogen oxide (NOx) indoor/outdoor concentration at naturally ventilated school building.

A.5 Indoor-outdoor source prediction (heating system and ventilation – indoor NO source)

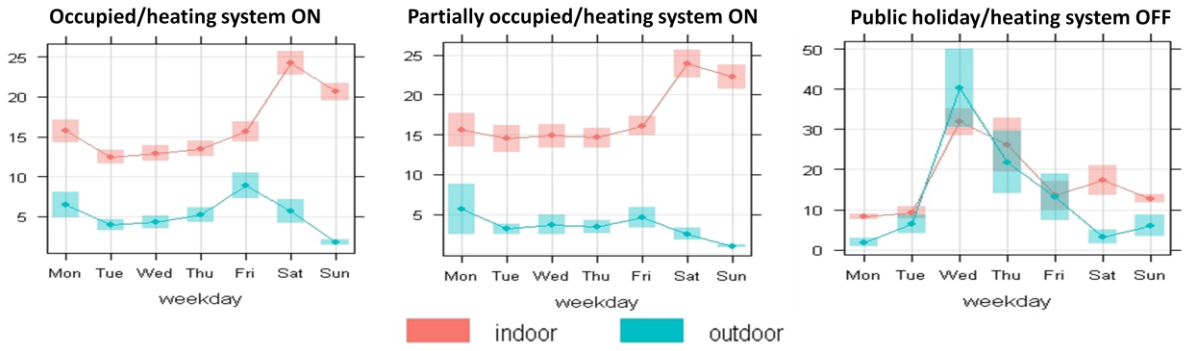


Figure A.4: Indoor and outdoor NO concentration according to building heating/ventilation and building occupancy

APPENDIX B: An assessment of indoor-outdoor pollutant at mechanically ventilated office building – roadside

B.1 Site and sampling description (TEOM PM_{10} &Osiris Dust monitor)

TEOM PM_{10} Osiris Dust monitor

Figure B.1: PM_{10} TEOM - LAQN CT8 site located at Upper Thames Street and PM Osiris Dust monitor was installed at main entrance.

B.2 Long term indoor-outdoor monitoring database

Monitoring at this site ran from August 2008 until June 2011, including additional study phase between March – June 2011 (gaseous pollutant species and airborne particulate). Data summary analysis was capture from analysers and data analysed using R statistical graphical plot.

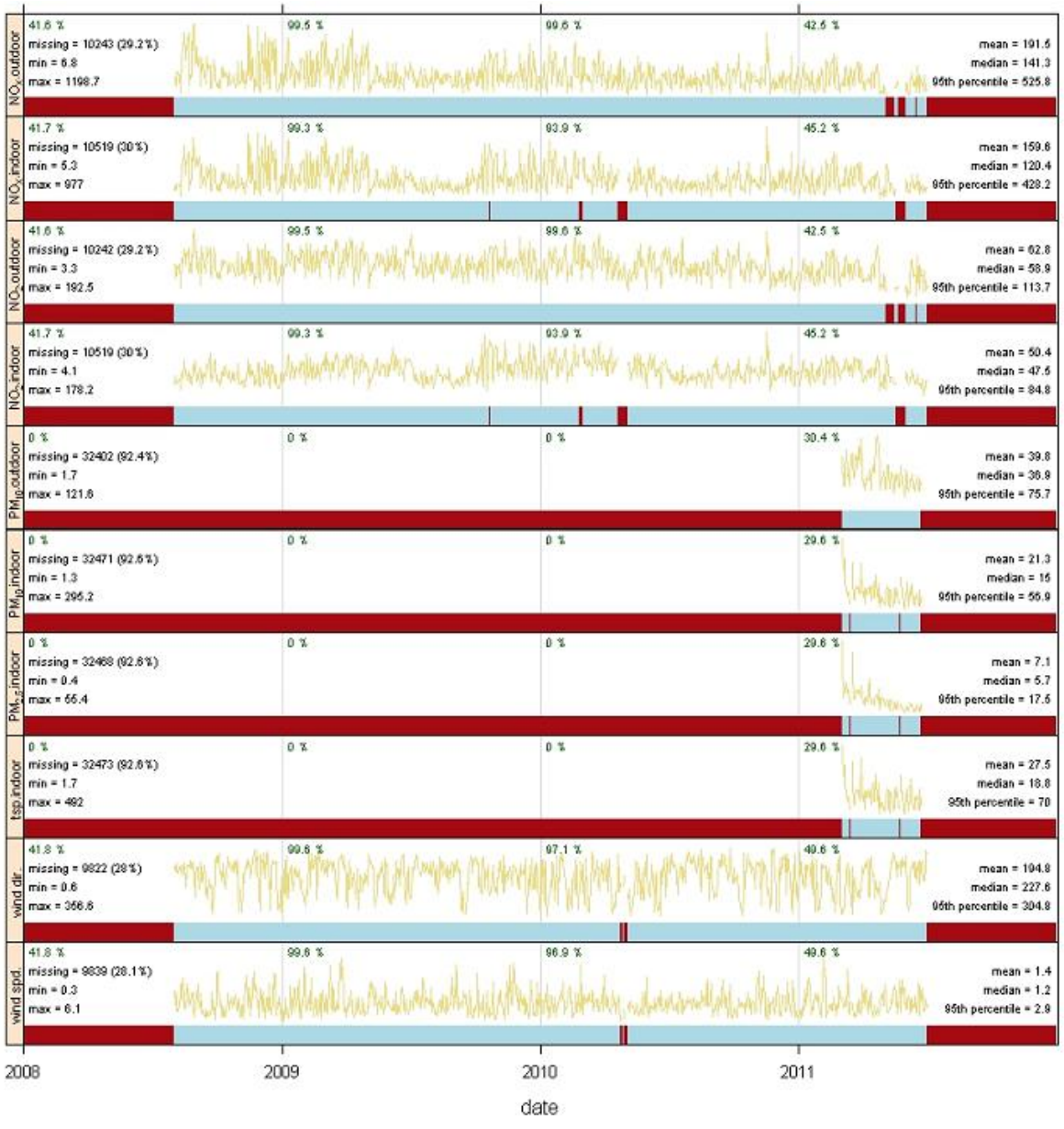


Figure B.2: Data summary plot for indoor-outdoor gaseous pollutants & particulate matter species monitored from August 2008 until June 2011

B.3 Meteorological condition (PM_{10})

The characteristics of indoor and outdoor PM_{10} distribution was analysed using R statistical graphical polar frequency plot to illustrated mean PM_{10} concentration associated with binned wind direction and wind speed measurements. The colour scale contrast between indoor-outdoor PM_{10} showed the hourly mean PM_{10} had different pattern of distribution. The results illustrated that the increment of indoor PM_{10} did not influenced by meteorological condition factors.

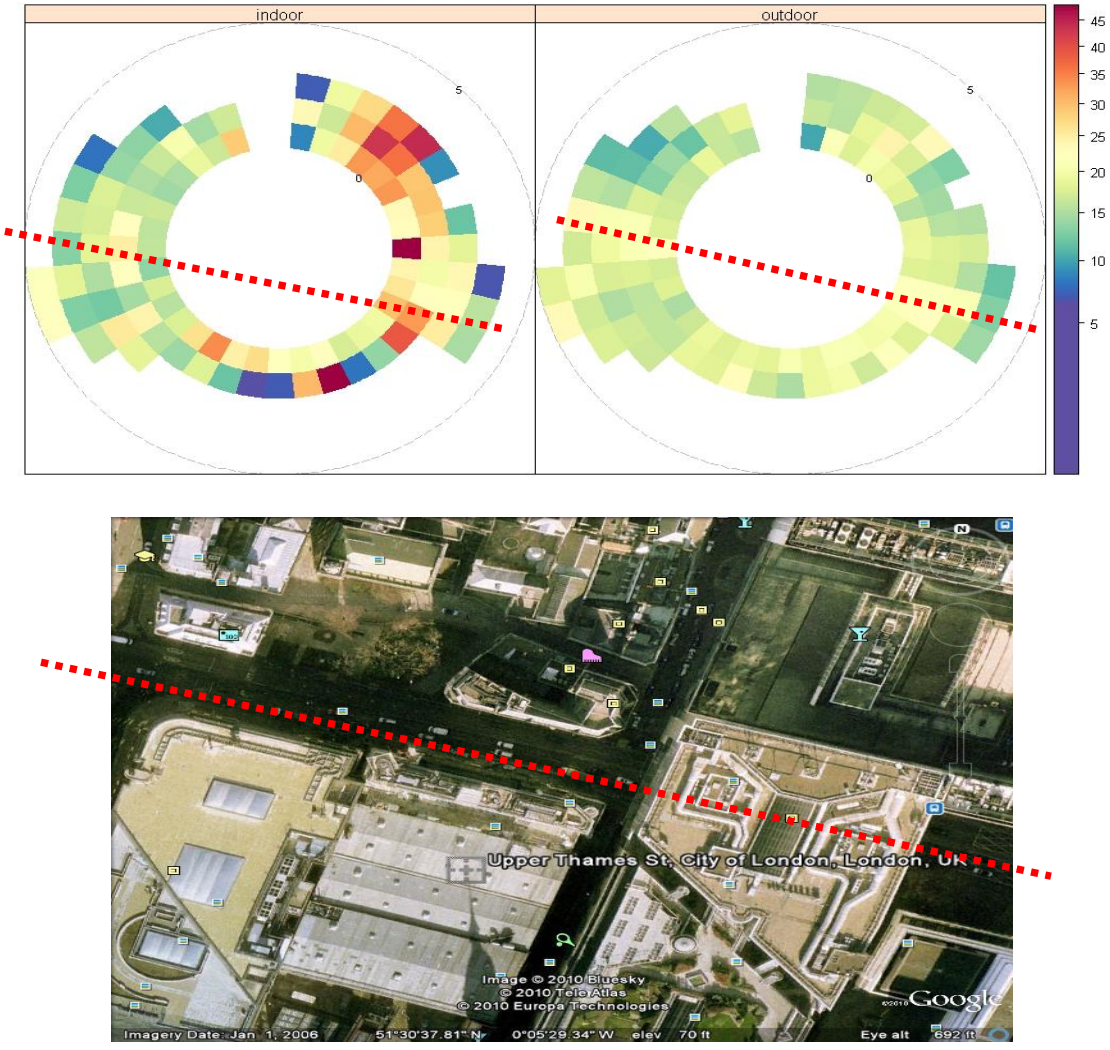


Figure B.3: Polar frequency plot between indoor-outdoor PM_{10}concentration at mechanically ventilated office building. The dashed line indicates the orientation of the adjacent road (Upper Thames Street).

Notes: Colour contrast represents pollutants concentrations in µg m^{-3}. Dotted red line shows roadside orientation at north side mechanically ventilated office building.

B.4 Seasonal variation (NO_X)

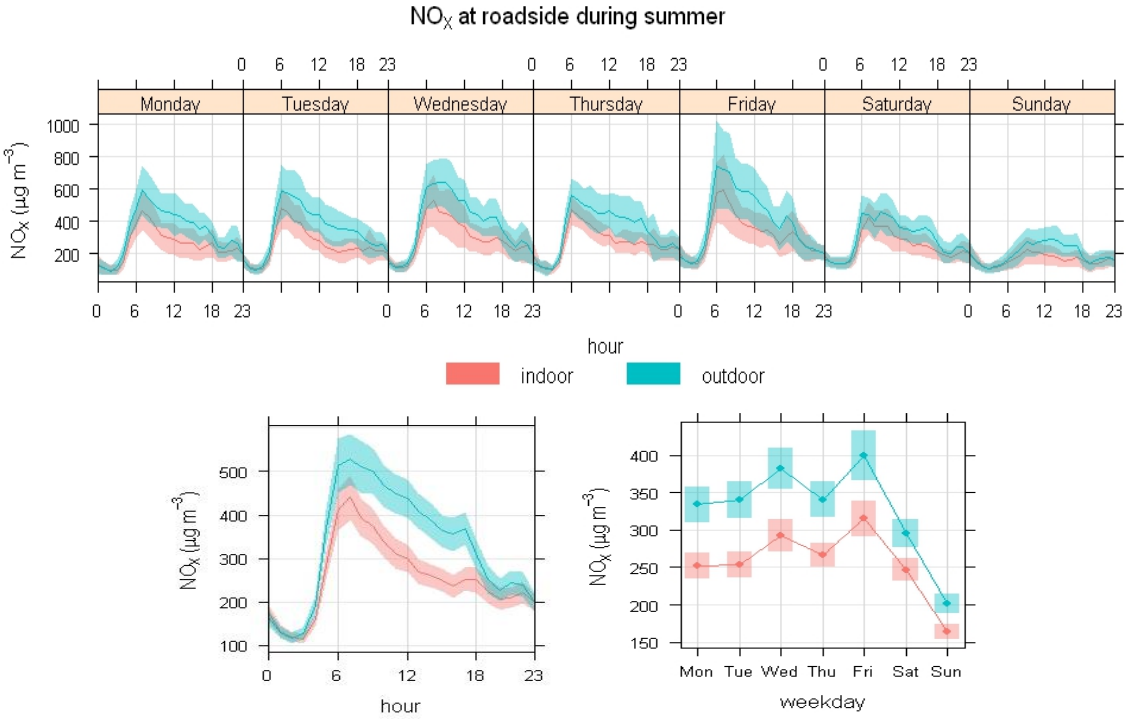


Figure B.4: Diurnal variation profile (hourly-weekly) represents the concentration between indoor and outdoor NO_X during summer

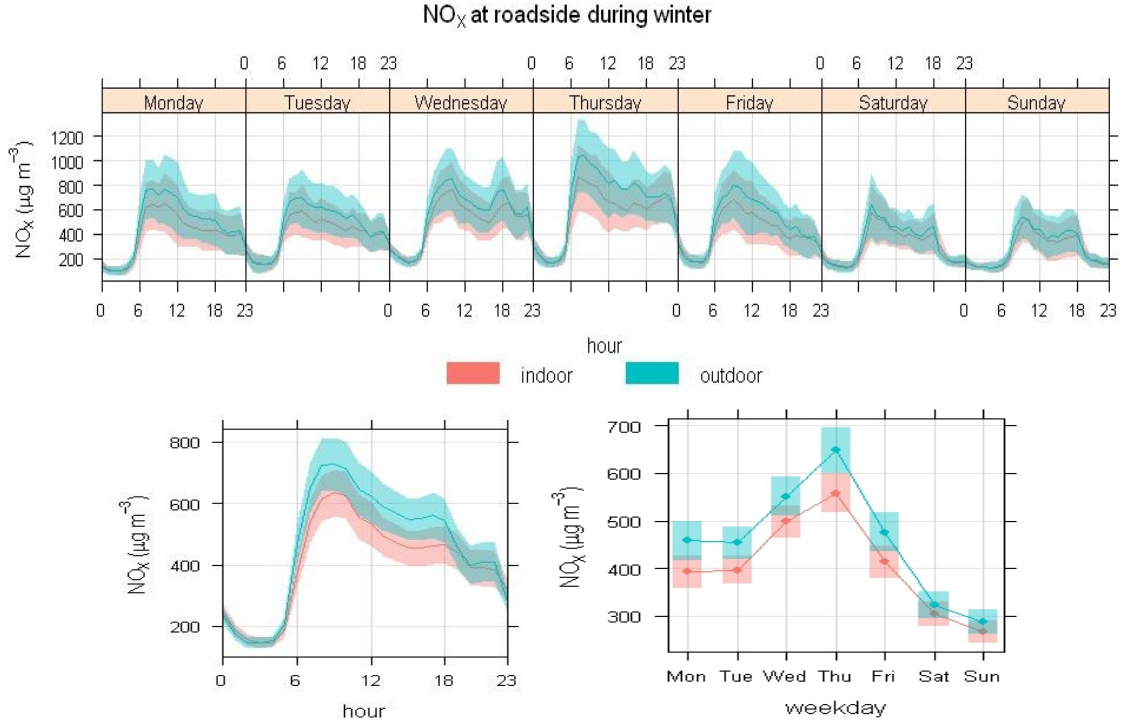


Figure B.5: Diurnal variation profile (hourly-weekly) represents the concentration between indoor and outdoor NO_X during winter

APPENDIX C: Characteristics of indoor-outdoor particulate oxidative activity at two contrasting buildings in London

C.1 The relationship between indoor-outdoor PM OP metric and mean gaseous pollutant species

Table C.1: Spearman's correlation between OP^{AA} and OP^{GSH} (μg^{-1} and m^{-3}) of PM samples and mean gaseous pollutant concentration ($\mu g\ m^{-3}$) in both study sites (urban background & roadside sites).

- Naturally ventilated school building (urban background)– NO_X, NO_2& O_3

Gaseous pollutants & sampling inlets		$OP^{AA}\ ug^{-1}$		$OP^{GSH}\ ug^{-1}$		$OP^{AA}\ m^{-3}$		$OP^{GSH}\ m^{-3}$	
		Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
NOx	Indoor	0.624		0.430		-0.649		-0.444	
	Outdoor		-0.080		0.312		-0.087		0.234
NO_2	Indoor	0.002		0.375		-0.564		-0.308	
	Outdoor		-0.051		0.240		-0.084		0.148
Ozone	Indoor	-0.320		0.048		0.009		0.172	
	Outdoor		-0.428		-0.138		-0.565		-0.318

- Mechanically ventilated office building (roadside) – NO_X, NO_2&NO

Gaseous pollutants & sampling inlets		$OP^{AA}\ ug^{-1}$		$OP^{GSH}\ ug^{-1}$		$OP^{AA}\ m^{-3}$		$OP^{GSH}\ m^{-3}$	
		Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
NOx	Indoor	0.643		-0.054		0.571		-0.487	
	Outdoor		0.180		-0.259		0.360		0.018
NO_2	Indoor	0.571		-0.180		0.536		-0.543	
	Outdoor		0.180		0.408		0.577		0.709
NO	Indoor	0.750		0.036		0.679		-0.674	
	Outdoor		0.180		-0.259		0.360		0.018

Data are represented as means +- SD (n=3). Based on correlation with spearman's output, there is no clear evidence of significant values on any gaseous pollutants ($p > 0.05$).

C.2 PM_{TSP} filter extraction mass obtained from both site study campaign (urban background & roadside site)

Table C.2: Date of filter collection from urban background site and extracted PM mass obtained during PM OP filter extraction – methanol procedure

Filter No	Sampling	Exposure Period	Extracted Mass (mg)
Os 1	Indoor	9-16 Mar	0.12
Os 2	Outdoor	*(1 week)*	0.03
Os 3	Indoor	17-24 Mar	0.51
Os 4	Outdoor	*(1 week)*	0.15
Os 5	Indoor	24-30 Mar	0.35
Os 6	Outdoor	*(1 week)*	0.30
Os 7	Indoor	30 Mar-6 Apr	0.24
Os 8	Outdoor	*(2 weeks)*	0.12
Os 9	Indoor	7-20 Apr	0.75
Os 10	Outdoor	*(2 weeks)*	0.65
Os 11	Indoor	20 Apr-4 May	0.63
Os 12	Outdoor	*(2 weeks)*	0.38
Os 13	Indoor	4-19 May	0.53
Os 14	Outdoor	*(2 weeks)*	0.38
Os 15	Indoor	19 May-1 June	0.86
Os 16	Outdoor	*(2 weeks)*	0.76
Os 17	Indoor	1 June-14 June	1.21
Os 18	Outdoor	*(2 weeks)*	1.28
Os 19	Indoor	14 June-29 June	2.16
Os 20	Outdoor	*(2 weeks)*	0.14
Os 21	Indoor	29 June-15 July	1.12
Os 22	Outdoor	*(2 weeks)*	0.47
Os 23	Indoor	15-27 July	3.10
Os 24	Outdoor	*(2 weeks)*	1.05
Os 25	Indoor	27 Jul- 10 Aug	2.85
Os 26	Outdoor	*(2 weeks)*	1.98
Os 27	Indoor	10 Aug-26 Aug	0.42
Os 28	Outdoor	*(2 weeks)*	0.36
Os 29	Indoor	2 Sept-19 Oct	1.06
Os 30	Outdoor	*(2 weeks)*	0.99
Os 31	Indoor	20 Oct -3 Nov	0.26
Os 32	Outdoor	*(2 weeks)*	0.25
Os 33	Indoor	4- 15 Nov	0.39
Os 34	Outdoor	*(2 weeks)*	0.27

Os 35	Indoor	16 Nov-7 Dec	0.35
Os 36	Outdoor	*(2 weeks)*	0.14
Os 37	Indoor	8-21 Dec	0.72
Os 38	Outdoor	*(3 weeks)*	0.36
Os 39	Indoor	*22 Dec – 12 Jan*	0.46
Os 40	Outdoor	*(2 weeks)*	0.31
Os 41	Indoor	13-27 Jan	0.26
Os 42	Outdoor	*(2 weeks)*	0.25
Os 43	Indoor	28 Jan- 8 Feb	0.39
Os 44	Outdoor	*(2 weeks)*	0.27
Os 45	Indoor	9-23 Feb	1.02
Os 46	Outdoor	*(2 weeks)*	0.36
Os 47	Indoor	24 Feb- 9 Mar	1.06
Os 48	Outdoor	*(2 weeks)*	1.39
Os 49	Indoor	10- 24 Mar	0.86
Os 50	Outdoor	*(2 weeks)*	0.25

Table C.3: Date of filter collection from roadside site and extracted PM mass obtained during PM OP filter extraction – methanol procedure

Filter No	Sampling	Exposure Period	Extracted Mass (mg)
Os 1	Indoor	17-24 Feb	0.98
TEOM 1	Outdoor	*(1 week)*	1.95
Os 2	Indoor	24 Feb-7 Mar	1.52
TEOM 2	Outdoor	*(1 week)*	2.30
Os 3	Indoor	7-16 Mar	0.32
TEOM 3	Outdoor	*(1 week)*	0.98
Os 4	Indoor	17-28 Mar	0.65
TEOM 4	Outdoor	*(1 week)*	1.12
Os 5	Indoor	28 Mar- 4 Apr	0.65
TEOM 5	Outdoor	*(1 week)*	1.32
Os 6	Indoor	5-12 Apr	0.98
TEOM 6	Outdoor	*(1 week)*	1.15
Os 7	Indoor	13-20 Apr	0.59
TEOM 7	Outdoor	*(1 week)*	0.98

C.3 PM $_{TSP}$ induced antioxidants (samples from urban background & roadside site)

Figure C 1.1 and C 1.2 shows the site/collection variation indoor-outdoor in PM $_{TSP}$ oxidative activity –antioxidants (AA and GSH) remaining in synthetic RTLF after 4 hour incubation in presence of PM $_{TSP}$ from both site study campaign (naturally ventilated school building – urban background & mechanically ventilated office building – roadside). Antioxidant controls at time 0hr and 4hr, as well as particle controls M120 (black hatched) and NIST (white hatched) are also illustrated. Statistical comparisons of the AA concentrations were performed using a one way ANOVA, with post hoc analysis performed with Games Howell test for groups with unequal size and variance. Where data are marked with an ** indicate significant difference to the 4hr control. Data are represented as means ± SD (n=3).

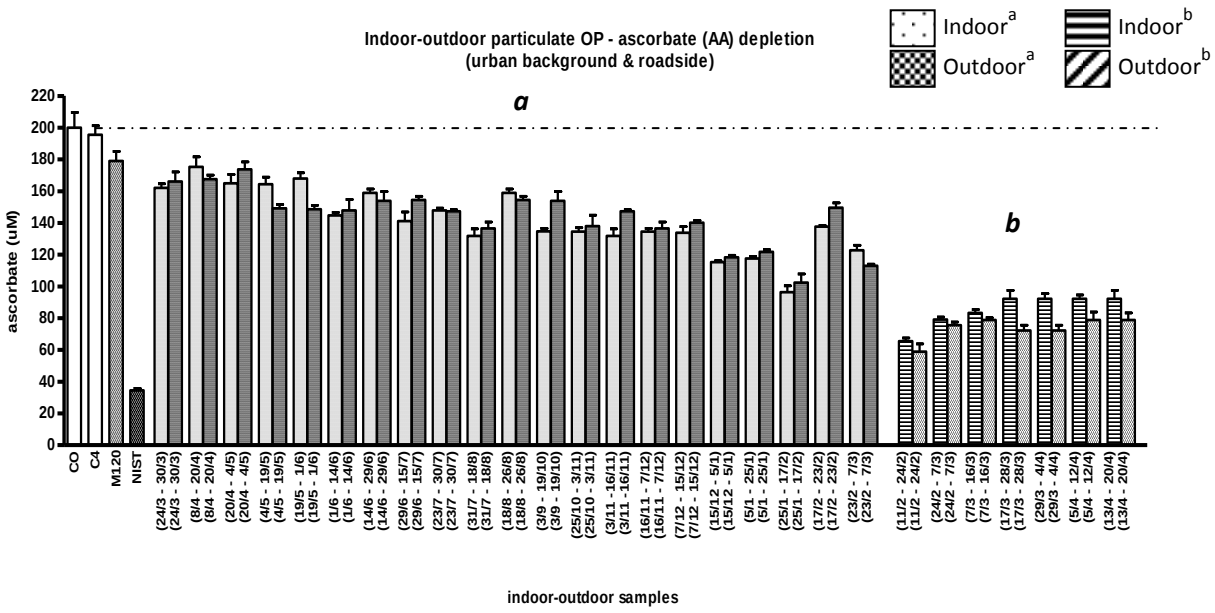


Figure C.1: Site/collection variation indoor-outdoor in TSP PM oxidative activity: AA depletion.

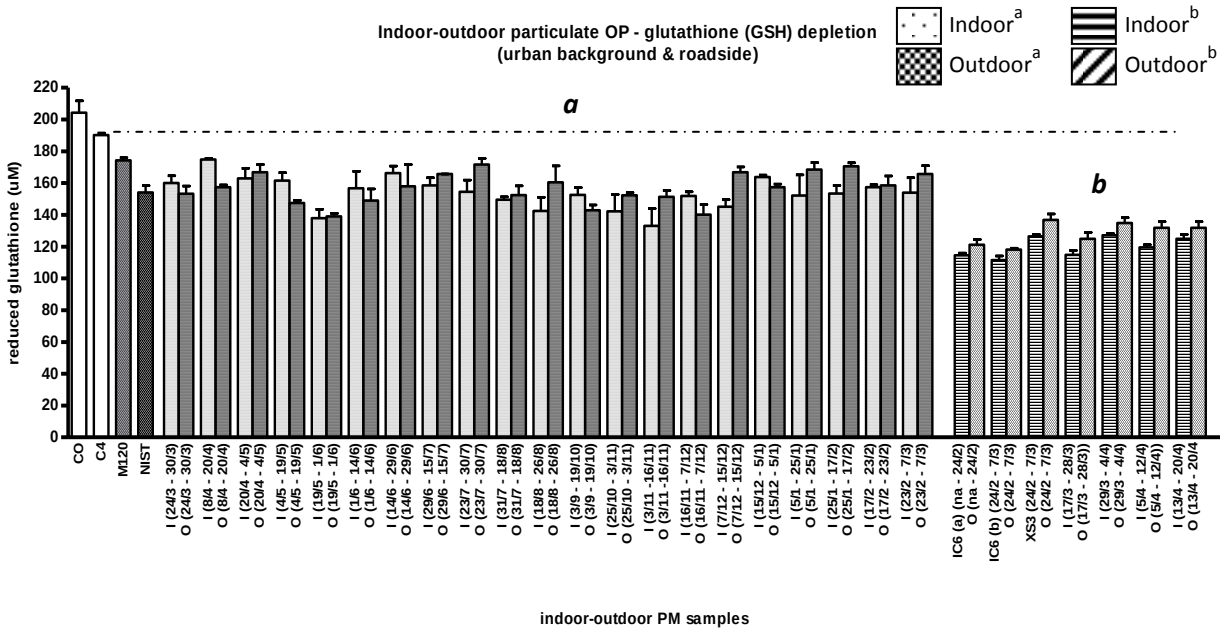


Figure C.2: Site/collection variation indoor-outdoor in TSP PM oxidative activity: GSH depletion.

C.4 QA/QC: Re-extraction of PM $_{TSP}$filter

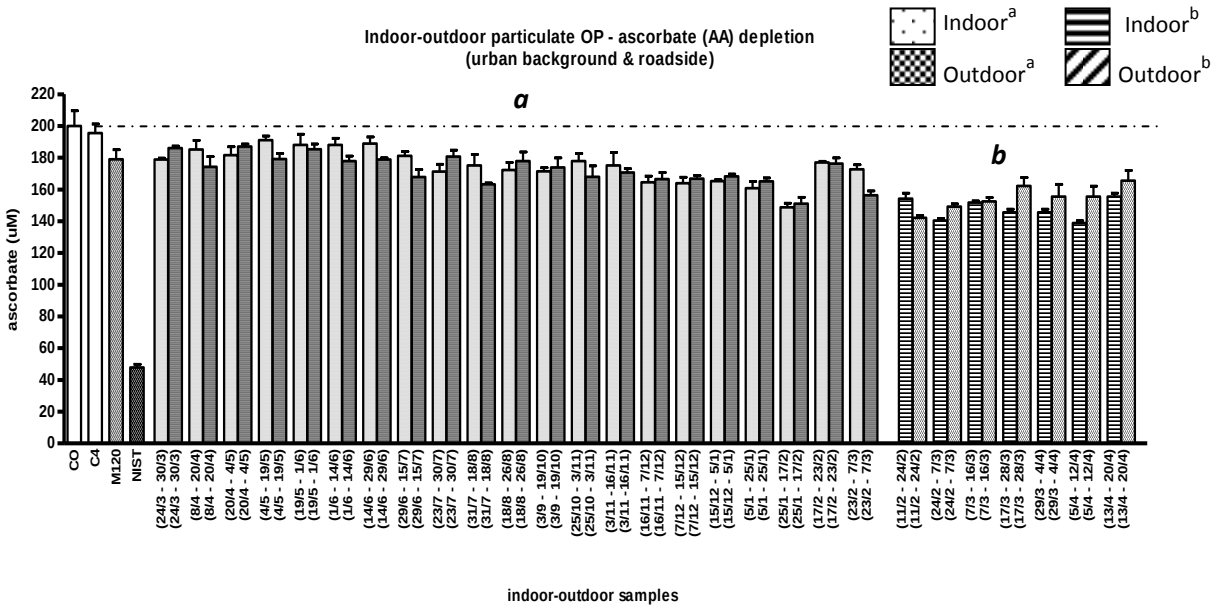


Figure C.3: Re-extraction PM $_{TSP}$ filters: AA depletion

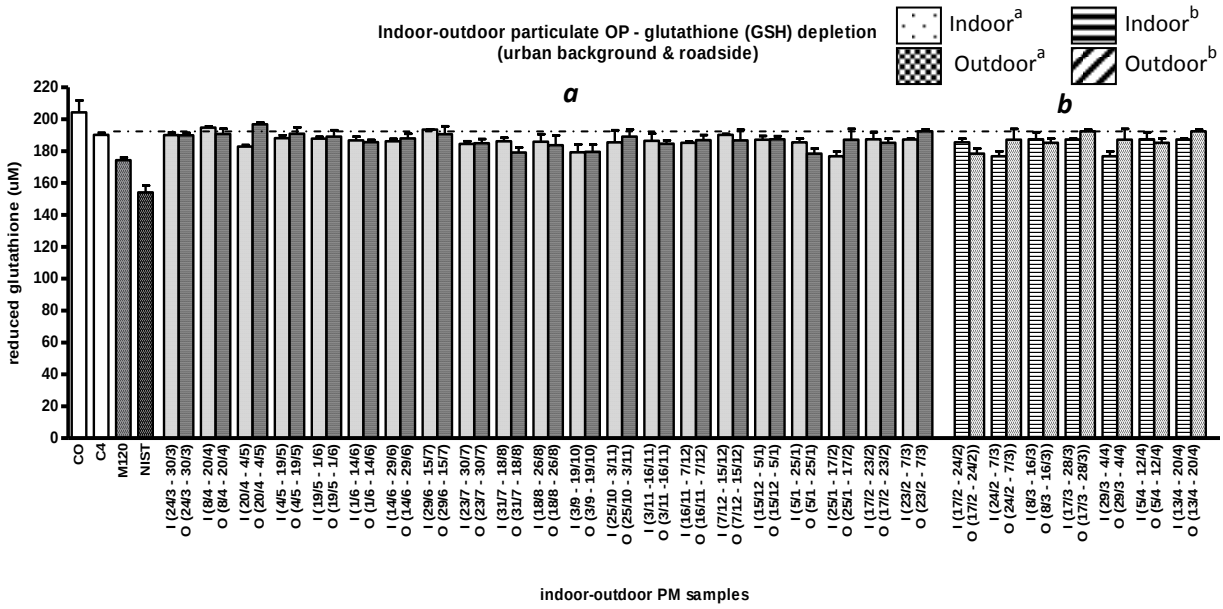


Figure C.4: Re-extraction PM $_{TSP}$ filters: GSH depletion

C.5 QA/QC: PM OP metric comparison between different types of filter collection from both sites study campaign

(PM $_{TSP}$& TEOM FDMS PM_{10}& $PM_{2.5}$ – urban background and PM $_{TSP}$& TEOM PM_{10} – roadside)

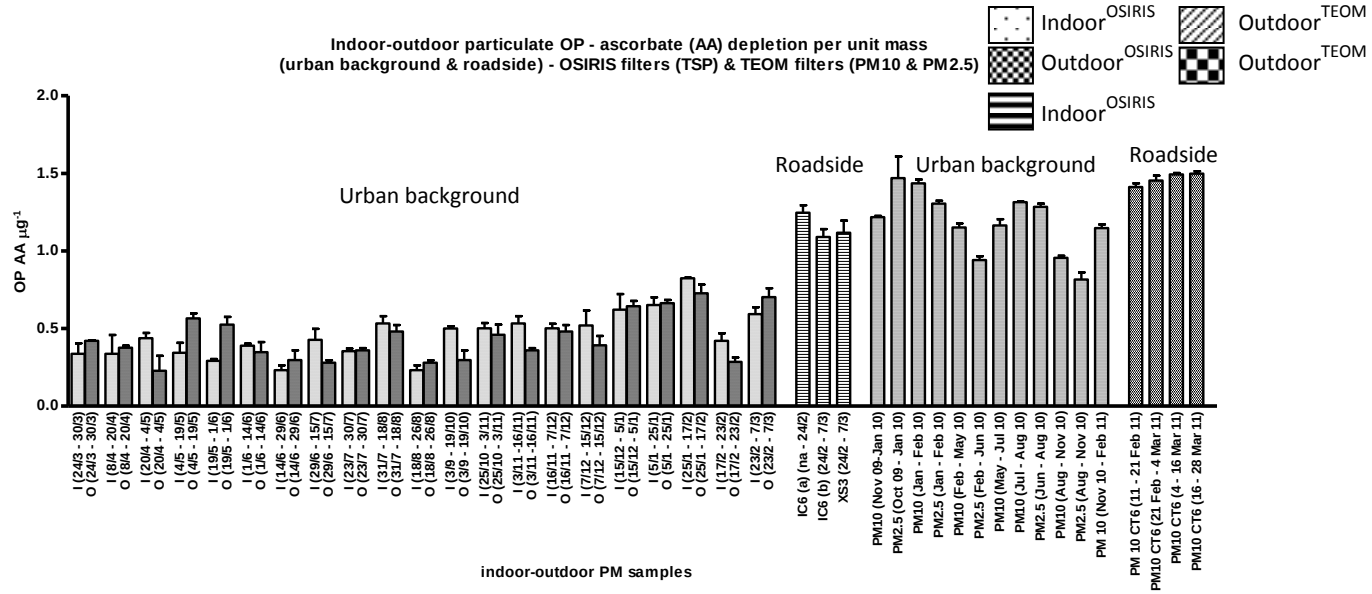


Figure C.5:PM OP ^{AA} µg $^{-1}$ comparison between different filter types of filter collection

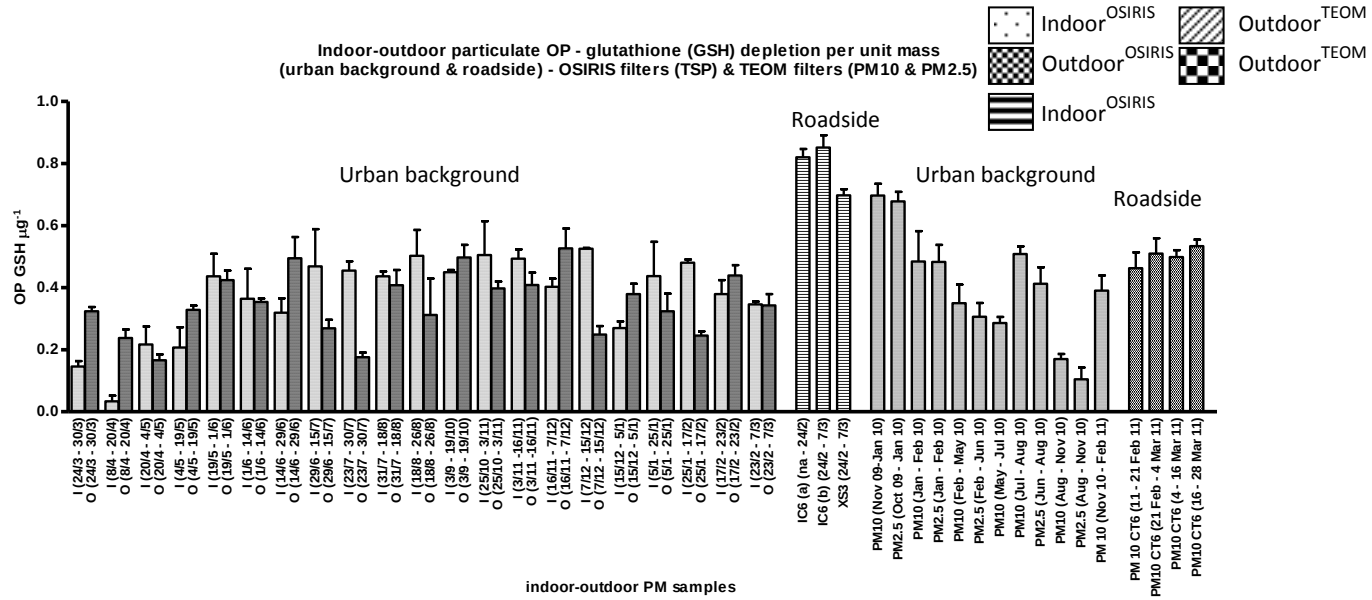


Figure C.6:PM OP ^{GSH} µg $^{-1}$ comparison between different filter types of filter collection

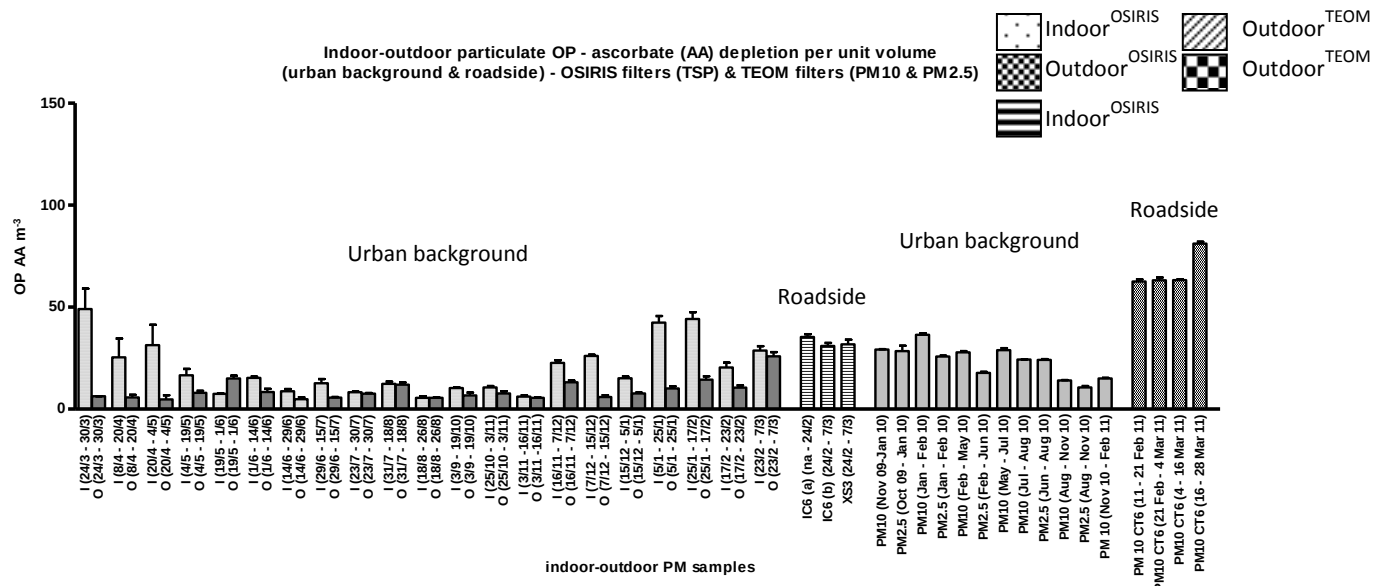


Figure C.7:PM OP ^{AA} m $^{-3}$ comparisons between different filter types of filter collection

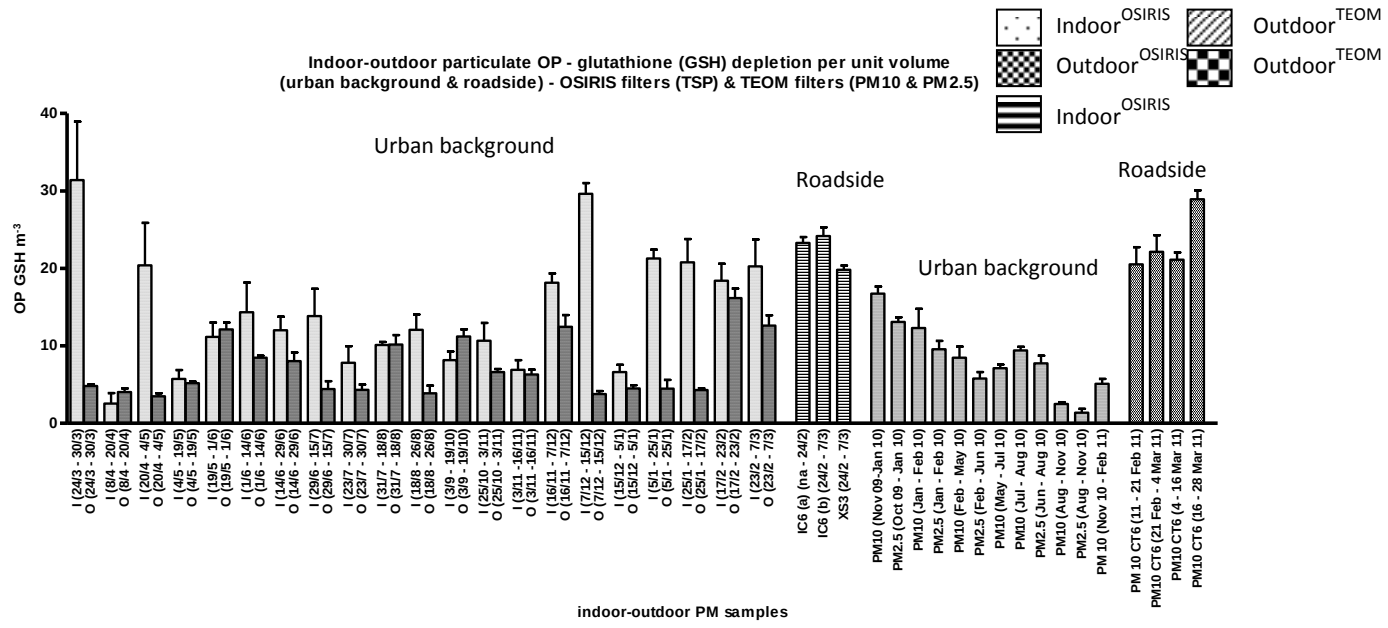


Figure C.8: PM OP ^{GSH} m $^{-3}$ comparisons between different filter types of filter collection